STUDIES ON SYNTHETIC INORGANIC ION-EXCHANGERS

SUMMARY

THESIS SUBMITTED FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

CHEMISTRY

BY

BALBIR SINGH

DEPARTMENT OF CHEMISTRY
ALIGARH MUSLIM UNIVERSITY
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The thesis entitled, "Studies on synthetic inorganic ion exchangers" is comprised of 5 chapters. Chapter I is general introduction covering the literature, to date through available journals, on the subject. The emphasis has been given on the importance of ion exchange as an analytical technique. Overall the introduction covers a critical review of the earlier work done on inorganic ion exchangers, their characterization, applications and main interest towards the mechanism of ion exchange and ion exchange equilibria. Looking for the growing interest in the physical chemistry of ion exchange, the emphasis has been put on the thermodynamics and kinetics of ion exchange.

The second chapter deals with the, "Ion exchange equilibria of alkali metal ions on ferric antimonate". Because inorganic ion exchangers have a rigid structure, they swell to a negligible extent and, therefore, the thermodynamic studies on inorganic ion exchangers will be simpler than that on their organic counterparts which have appreciable swelling. The influence of temperature on the ion exchange equilibria of Li^+, Na^+, K^+ and Rb^+ with H^+ has been described in this chapter for a temperature variation of 30 to 60 $^{\circ}C$. The thermodynamic parameters, ΔG°, ΔH° and ΔS° have been evaluated. The equilibrium experiments were performed by a batch process equilibrating for 6 hours at desired temperatures. The exchange isotherms are plotted for the said ions and the results indicate

a differential selectivity with a reversible exchange process

$$\bar{H}^+ + M^+ \rightleftharpoons \bar{M}^+ + H^+$$

where M^+ stands for an alkali metal ion and bar represents the exchanger phase. The selectivity coefficients have been calculated by the experimental results and the thermodynamic parameters then calculated using appropriate equations. The hypothetical data at "zero loading" have also been evaluated.

The third chapter deals with the, "Ion exchange equilibria of $Cr_2O_7^{2-}$, CrO_4^{2-}, $S_2O_3^{2-}$, SO_4^{2-} and MnO_4^- with NO_3^- on zirconium triethylamine". The survey of the earlier literature shows that only a few thermodynamic studies have been made on inorganic anion exchangers. This chapter describes the thermodynamic studies on a new inorganic ion exchanger, zirconium triethylamine. A simple approach has been applied using a batch process for equilibrium based on the mass action law modified in terms of activities. The various isotherms plotted indicate that the bivalent anions are preferred to nitrate ions by the zirconium triethylamine exchanger. All the isotherms show reversibility of ion exchange whereas the selectivity sequence is

$$Cr_2O_7^{2-} > CrO_4^{2-} > S_2O_3^{2-} > SO_4^{2-} \gg MnO_4^-$$

The results of the selectivity coefficients indicate that the

value of selectivity coefficient decreases as the temperature increases. The thermodynamic parameters are evaluated by the thermodynamic equilibrium constant.

The fourth chapter describes the, "Ion exchange kinetics of transition metal ions on stannic oxide". Kinetics play an important role to study the mechanism of ion exchange. The mechanism has been found to be a particle diffusion control. A theoretical approach based on certain calculations has been applied. The energy of activation and other parameters are evaluated. The studied ions are Fe^{3+}, Mn^{2+}, Co^{2+} and Zn^{2+} with H^{+} exchange. The studies on effect of temperature show that the rate of exchange increases as the temperature increases. Besides the temperature the exchange also depends upon the particle diameter and time.

The last chapter i.e. the V chapter describes the synthesis, properties and applications of a new inorganic anion exchanger, ferric triethylamine. Ion exchange capacity, composition, chemical stability, effect of heat on capacity, pH-metric titrations have been studied to characterize the new material. IR studies have been made to confirm the presence of various groups. Distribution studies for 17 common anions have been made. The utility of the exchanger has been explored by achieving some analytically important separations.

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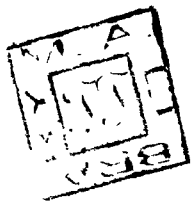

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CERTIFICATE

This is to certify that the work embodied in this thesis is original and suitable for submission for the award of Ph.D. degree in Chemistry.

J.P.RAWAT

DEDICATED TO MY PARENTS

A C K N O W L E D G E M E N T

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Balbir Singh

/ BALBIR SINGH /

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   BULL.CHEM.SOC.JAPAN, 57, 271 (1984).

2. ION EXCHANGE KINETICS OF TRANSITION METAL IONS ON STANNIC OXIDE.
   J.INDIAN CHEM.SOC., (IN PRESS).

3. ION EXCHANGE EQUILIBRIA OF $Cr_2O_7^{2-}$, CrO_4^{2-}, $S_2O_3^{2-}$, SO_4^{2-} AND MnO_4^- WITH NO_3^- ON ZIRCONIUM TETRAETHYLAMINE.
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INTRODUCTION

Analytical chemistry plays an important role in the scientific world. It is the key to the solution of a variety of scientific problems. Analytical chemistry with its interdisciplinary character, gives valuable information in many branches of science and technology. It determines the qualitative and quantitative composition and structure of chemical systems and participates in the interpretation of the data obtained.

Analytical chemistry has two faces: (i) research and development, and (ii) using routinely as a working tool in research, industry and medicine. An analyst must use its methods, while an analytical chemist has to interface with many different disciplines to interpret the results he obtains. For an analysis some form of pretreatment of sample is usually required so as to remove the interference of other substances. Separation, in most of the cases, is one of the important methods of pretreatment and involves classical and modern techniques. The precipitation and distillation are the classical techniques and are replaced markedly by modern techniques as solvent extraction, ion-exchange, chromatography, electrometric titrations etc. The rapid development of these modern techniques has increased the requirements placed in analytical laboratories.

At present ion-exchange is an extremely valuable analytical technique. The ion-exchangers had a great impact on analytical chemistry. The use of these materials gave analysts new methods for the requirements of modern laboratories. Using inorganic and organic exchangers we can have a deeper understanding of geological, geophysical and biophysical phenomena to explain the biological process. In laboratory, the application of ion-exchangers has made possible the chromatographic separation of very complicated natural mixtures. The time is much reduced by the use of high performance chromatographic techniques. Their use has also been made to the solution of previously unsolvable problems. Such as the separation of rare earths and recovery of rare elements. The atomic power control laboratories and many different industrial laboratories are now unimaginable without the use of ion-exchangers. The ion-exchange separations offer advantages over the classical methods of separations (precipitation, filtration etc.) for the amount of the sample required is small, a shorter time is needed and the components can subsequently be determined using rapid instrumental or titrimetric methods. Rapid and accurate determination of constituents of a sample or, contaminents of alloys of complicated compositions, biological substances and fission products of radioactive elements has become possible by the use of ion-exchangers. Ion-exchange

chromatography can be routinely used to overcome interactions and troubles in the determination of trace elements of geochemical interest, before optical or atomic absorption spectrophotometry and neutron activation analysis[1]. Ion-exchange materials are finding increased use in gas-chromatography because they offer a great range of potential selectivity through variation of the ionic form of material[2]. All over the world numerous ion-exchanger plants are in operation for developing the separations of inorganic, organic and biological mixtures. The most important application is still the purification of water. The water pollution is increasing day by day. However, the methods based on ion-exchange are becoming of promising success when applied to this field. The use of ion-exchangers on large scale may provide mankind with pure water and may be useful for the concentration and extraction of the most important metals and raw materials which is becoming more and more difficult to produce.

Ion-exchange was recognised in the middle of the last century following the investigations of two agricultural chemists, Thomson[3] and Way[4] who were studying the uptake of fertilizers by soils. They discovered this phenomenon by the name of "base exchange" in soils. The exchange involved equivalent quantities of replaceable and replaced ions. It was established in 1854 that aluminium silicates were responsible for this exchange[5,6]. According to Lamberg[7] and

Weigner[8] the materials responsible for this phenomenon were defined mainly clays, zeolites, gluconites and humic acids. These discoveries led to the use of the natural materials for water softening. The first synthetic industrial ion-exchanger was prepared by Harm and Rumpler[9] in 1903. Gans was ambitious to recover gold from sea water adopting this technique. But he could not fulfil his ambitions because the material of this type available at that time proved to be inadequate for the purpose. Gans, however, recognised the practical utility of the ion-exchange phenomenon for water softening using natural and synthetic zeolites and clays[10]. The exhausted bed of the ion-exchanger was regenerated by passing a concentrated solution of sodium or, potassium salt over it. Because of this possible regeneration these zeolites and clays were soon recognised i.e. zeolites are decomposed by acids and clays are difficult to handle. To overcome these difficulties a search of stable ion-exchange materials was started. In 1931 Kullgren[11] observed that sulphite cellulose works as an ion-exchanger for the determination of copper. An interesting discovery began in 1935 when Adams and Holmes found that crushed phonograph records exhibit ion-exchange properties. The remarkable effect led the inventors to the synthesis of organic ion-exchange resins which had much better properties than any of the previous

products[12]. These resins are stable towards acids and easy to handle. The structure can be varied as desired, therefore, the difficulties observed with zeolites and clays were removed by introduction of resins. Since then these organic ion-exchangers have been used both in laboratories and industries for separations, recoveries of metals, deionization of water, concentration of electrolytes and elucidating the mechanism of great many reactions[13]. The applications of these ion-exchange resins progressed so rapidly that the theory lagged behind and could not follow the experiments.

Just as the applications of the zeolites are limited so are those with organic ion-exchange resins under certain conditions. The resins are unstable in aqueous systems at high temperatures and in presence of ionizing radiations. For these reasons there has been a resurgence of interest in inorganic ion-exchangers in recent years as they are unaffected by ionizing radiations and are less sensitive to higher temperatures. The structure of these inorganic ion-exchangers is stiff, therefore, they are more selective and suitable for the separation of ions on the basis of their different pore sizes. They can also be used as ionic or molecular sieves. Being stable towards ionizing radiations, they can be used advantageously in reactor technology. Inorganic ion-exchange membranes have also recently been used preferably over

organic ones because of the inorganic membranes could permit higher temperatures to be used and higher selectivity for certain ions.

The selectivity of inorganic ion-exchangers has been utilized for the preparation of ion selective electrodes[14]. The ion selective electrodes have now become important tool for solving various analytical problems[15-17].

In order to understand the applications and to improve upon them, systematic fundamental studies are being pursuaded on these materials. This new interest in inorganic ion-exchangers may be said to begin in 1945. It was shown by Boyd[18] that columns containing finally divided zirconium phosphate supported on silica wool could be used to seperate uranium and plutonium from fission products by an ion-exchange process. In addition to zirconium phosphate many other similar substances may be prepared by combining oxides of group IV with the more acidic oxides of groups V and VI of the periodic table.

The various inorganic ion-exchangers reported upto 1963 have been admirably reviewed in the monograph of Amphlett[19] which has become a classic in this field. The studies on these materials from 1963-1969 have been summarized by Dakarek and Vesely[20,21] under the following heads:

1. Hydrous oxides,
2. Acidic salts of multivalent metals,
3. Salts of heteropolyacids,
4. Insoluble ferrocyanides,
5. Synthetic aluminosilicates, and
6. Certain other substances e.g. synthetic apatites, sulphides and alkaline earth sulphates.

Marinsky has summarized the theoretical aspects of exchange in inorganic ion-exchange materials[27]. The synthesis and applications of inorganic ion-exchangers have been reviewed by Walton[22-26]. Recent review on the applications of ion-exchange have been edited by Marinsky[28] and Walton[29]. The recent trends in the field of ion-exchange have been summarised in the Journal of Chromatography volume 102 (1974) which contains the papers presented at the third symposium on ion-exchange held at Balatonfüred (Hungry) May 28-31,1974. The papers presented were divided into four sections: (i) ion-exchange materials, (ii) theory of ion-exchange, (iii) analytical applications, and (iv) ion-exchange technology.

The synthesis of new materials have been reported by numerous authors defining different types of amorphous, poorly crystalline and crystalline materials. The theory of ion-exchange and the use of ion-exchangers in laboratories and

factories is a flourishing discipline. The applications of ion-exchangers in the laboratories as made possible, the chromatographic separation of very complicated mixtures. The selective use of inorganic ion-exchangers may provide a useful means to concentrate and extract the most important metals from laboratories wastes and local concentrated samples. The applications of ion-exchange to some important processes that occur at high temperatures or in the presence of ionising radiation or highly oxidising media are severely limited on commercially available ion-exchange resins. However, the use of synthetic inorganic ion-exchangers can be made under these conditions.

Until recently, the insoluble acid salts of polyvalent metals have been obtained as gelatinous substances. The zirconium phosphate is probably the first and the most studied of all the ion-exchangers. Crystallization of some of them have improved the chemical stability and reproducibility in the ion-exchange behaviour. Most of the ion-exchange materials with their properties are given previously[30].

For a complete description of a material as an ion-exchanger the following properties must be studied:

1. The ion-exchange capacity,
2. The resistance towards acids and bases,
3. Composition,

4. Potentiometric studies,
5. Distribution of counter ions between solution and exchanger phases,
6. Thermodynamics,
7. Kinetics, and
8. Analytical applications.

Ion-exchange capacity is one of the most fundamental quantities for characterization of any ion-exchange material. For a strong ion-exchanger, the capacity can readily be determined by direct titration. Various types of capacities can be expressed in different manners. The equilibrium ion-exchange capacity for a strong ion-exchanger can be determined by direct titration of strong cation exchanger (in H^+ form) with a strong base. Majority of the synthetic inorganic ion-exchangers behaves as a weak ion-exchanger and, therefore, the direct titration is not reliable. In this case ion-exchange capacity is determined by replacement of hydrogen ions from the exchanger phase by the counter ions of a neutral salt solution and of determining the equilibrium ion-exchange capacity is by pH-titrations. Maximum ion-exchange capacity equal to the numbers of ionogenic groups per specified amount of ion-exchanger may directly be determined by simple column operation passing the electrolytic solution over the ion-exchange material (in H^+ form) and titrating the liberated acid in the effluent by a standard base solution.

Although the pure ion-exchange capacity of a solid ion-exchanger can be determined in several ways, a gravimetric method[31] offers for many ion-exchangers the advantage of relatively high accuracy and very simple equipment requirements for only on difference weighing without any analytical chemical determination of ion. Break-through capacity[32] i.e. the useful capacity for utilizing the column operations, is of importance when the rate of exchange is slow. This rate may be slow that the total capacity may not be utilized in an actual operation. The operation is discontinued at break-through before reaching the complete equilibrium. This capacity which is utilized until break-through occurs is known as break-through capacity or dynamic capacity. It depends upon operating conditions and is lower than the equilibrium ion-exchange capacity.

The ion-exchange material must be studied for chemical stability in acidic and basic media to check its limitations.

Potentiometric titrations are helpful in finding whether the exchanger is monofunctional or polyfunctional. Alberti has studied titration curves in detail on zirconium phosphate with alkaline earth metal hydroxides[33]. He observed that these curves are strongly affected by hydrolysis of exchanger and precipitation of insoluble phosphates. He found that Ca^{2+} precipitates on the exchanger at 70° exchange,

Sr^{2+} at 80° exchange and Ba^{2+} at 100° exchange. No exchange was found with $Mg(OH)_2$ probably because the hydrated ion of Mg^{2+} is very large and it cannot penetrate in the cavity of the exchanger. He also studied the forward and reverse Na^+-K^+ ion-exchange isotherm[34] and found that Na^+-K^+ exchange in an aqueous solution is a two step process with partial phase solubility. Alberti also studied the ion-exchange on crystalline zirconium phosphate prepared either by the refluxing procedure or by direct precipitation procedure[35]. It was observed that two materials, although exhibiting similar x-ray powder patterns, possess different ion-exchange behaviour.

To understand the theoretical behaviour of ion exchange, thermodynamics is an important study to which some work should be devoted. Two different approaches have been applied for this purpose.

The first approach is based on the design of more and more elaborate models which have nearly like actual ion exchangers. The application is straight forward. This approach gives semiquantitative picture to a practical chemist who is interested in understanding the physical causes of the phenomena. However, the choice of the model is crucial and this approach is less likely to satisfy a theoretical chemist who is interested in a rigorous thermodynamic treatment.

In the second approach attempts have been made to correlate the activities with some measurable quantities with the thermodynamic equations. Some of the approaches of this kind may be mentioned. The earliest approaches were based on semiemperical or emperical equations to fit in experimental results. Probably, the first quantitative formation of ion exchange equilibria was made by Gans[36] using the mass action law in its simplest form. The formula did not involve the concept of activity coefficients. This concept was accounted by Kielland[37]. A suitable choice is the general treatment given by Gaines & Thomas[38].

Thus the most important treatment in ion exchange is the study of chemical equilibrium which, of course, is a study in thermodynamics. Inorganic ion exchangers offer the advantages for these studies because of their rigid structure, negligible swelling and differential selectivity. When an ion exchanger in counter ion A form is placed in a solution of counter ion B form, there will be an equilibrium set up for the distribution of A and B between the exchanger and solution phases according to their selectivity. This exchange (at equilibrium) may be represented as:

$$\bar{A} + B\,(aq) \rightleftharpoons \bar{B} + A\,(aq) \quad \ldots\ldots (1)$$

For the sake of convenience the effect of co-ions on the

equilibrium may be neglected. The thermodynamic equilibrium constant for this reaction may be written as:

$$K_a = \frac{\bar{a}_B \, a_A}{\bar{a}_A \, a_B} = \frac{[\bar{B}]\,[A]}{[\bar{A}]\,[B]} \times \frac{\gamma_B \, f_A}{\gamma_A \, f_B} \qquad \ldots\ldots \quad (2)$$

where γ represents activity coefficient in the exchanger phase and f, the activity coefficient in the aqueous phase.

The particular use of thermodynamic equilibrium constant is made to find out the free energy changes in the ion-exchange processes. The ionic selectivity is governed by the lowering of free energy of the system is an important factor which gives the information about the preferential uptake of the counter ion by the exchanger. Knowing K_a values at different temperatures the enthalpy change of the system may also be evaluated. The enthalpy change is the property most directly related to the changes in the numbers and strength of bonds in the ion-exchange reactions.

The ion-exchange reaction (equation 1) provides that structural changes within the exchanger are small, the most important factor influencing the entropy change in the reaction involving the exchange of equally charged ions will be expected to result from changes in liberation entropy may also play an important part, the overall entropy will reflect changes in randomness in the ion-exchange reaction, the driving forces

being the tendency for the system to go to the most probable, that is the most random state.

The ion-exchange equilibria of Li^+, Na^+, K^+ and Cs^+ was studied by Larsen and Vincero[39] and Gal and Ruvarac[40] on amorphous zirconium phosphate of various composition and properties. Recently, extention studies on the ion-exchange thermodynamics of alkali cations have been made with more defined semicrystalline and crystalline zirconium phosphate[41-51]. They interpreted the thermodynamic parameters in forms of nature of the bonding between the alkali metal ion and the matrix. Baetele[52] studied the exchange of Ca^{2+}, Sr^{2+}, Co^{3+} and Eu^{3+} ions with hydrogen both at micro and macro concentrations levels over a range of temperature (5-70 °C) on zirconyl phosphate. The exchange equilibrium studies of $Ca^{2+} - H^+$ [53] and $UO_2^{2+} - H^+$ [54] have been made by Ruvarac on crystalline zirconium phosphate. Recently the ion exchange equilibria on cobalt(II) hexacynoferrate(II) have been made by Cerenic and Adamovic[55]. Similar studies have also been reported on hydrous zirconia, anion exchanger, by Nancollas[56]. The thermodynamics of ion-exchange on zeolites have been made with a greater extent. R.M.Barrer, H.S.Sherry and A.Dyer studied the effect of temperature on ion-exchange with different zeolites in various cationic forms. They calculated the thermodynamic parameters. Thermodynamic studies for alkali metals and alkaline earth metals on ferric antimonate[57,58]

and niobium arsenate[59] were made in our laboratories. Some of the equilibrium studies on different ion exchange materials with various systems and their parameters are given in Table I.

TABLE I

THERMODYNAMIC STUDIES ON VARIOUS ION EXCHANGE MATERIALS

Sl. No.	Ion exchange material	Systems studied	Various parameters	References
1.	Crystalline α-zirconium phosphate	Na^+-Cs^+-H^+ exchange	Phases formed during the exchange at equilibrium	60
2.	Zirconium phosphate	UO_2^{2+}/H^+	K, ΔG, ΔH and ΔS	61
3.	Crystalline zirconium phosphate	Na^+/K^+, Na^+/Li^+, K^+/Li^+ and Na^+/Cs^+	Ion exchange isotherm and selectivity sequence $K^+ \rangle Cs^+ \rangle Na^+ \rangle Li^+$	62
4.	α-Zirconium phosphate	K^+/H^+	ΔG°, ΔH° and ΔS°	63
5.	Crystalline zirconium phosphate	Cs^+/H^+, Rb^+/H^+	Forward and reverse isotherms x-ray diffractogram	64
6.	α-Zirconium phosphate	K^+/Na^+	K, ΔG, ΔH and ΔS	65
7.	α-Zirconium phosphate	Li^+, Na^+, K^+/H^+	Isotherms and x-ray analysis	66
8.	α-Zirconium phosphate	Li^+, Na^+, K^+, Ca^{2+} and Sr^{2+}/H^+	Equilibrium and kinetic X-ray photographs	67
9.	Semicrystalline zirconium phosphate	Li^+, K^+ and Cs^+/H^+	ΔG°, ΔH° and ΔS°	71
10.	-do-	Cs^+/Rb^+, Cs^+/K^+	K, ΔG° and ΔH°	72

(Table I continued)

Sl. No.	Ion exchange material	Systems studied	Various parameters	References
11.	Semicrystalline zirconium phosphate	Cs^+/H^+ and H^+/Cs^+	K	70
12.	α-Zirconium phosphate	K^+/H^+	Completed layer structure	68
13.	-do-	Li^+/Cs^+, Na^+/Cs^+ and K^+/Cs^+	K, $\triangle G^\circ$ and $\triangle H^\circ$	69
14.	-do-	Cs^+/H^+	G° (298°C)	70
15.	Crystalline antimonic acid	H^+/Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Ca^{2+}	ln K, $\triangle G$, $\triangle H$ and $\triangle S$	73
16.	-do-	Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}/H^+	Selectivity sequence, reversibility X-ray studies	74
17.	-do-	Mg^{2+}, Sr^{2+}, Ca^{2+}, Ba^{2+} and Pb^{2+}/H^+	Kielland coefficient, $(\ln K_H^M)_{\bar{X}_M} \rightarrow 0$	75
18.	-do-	NH_4^+/H^+, $CH_3NH_3^+/H^+$, $C_2H_5NH_3^+/H^+$, $(CH_3)_2 NH^+/H^+$, iso-$C_3H_7NH_3^+/H^+$ and $(C_2H_5)_4 N^+/H^+$	ln K, $\triangle G$, $\triangle H$ and $\triangle S$	76
19.	-do-	H^+/Li^+, H^+/Na^+, H^+/K^+, H^+/Rb^+ and H^+/Cs^+	ln K, $\triangle G$ and x-ray studies	77

(Table I continued)

Sl. No.	Ion exchange material	Systems studied	Various parameters	References
20.	Ferric antimonate	H^+/Li^+, Na^+, K^+ and Rb^+	K, $\triangle G$, $\triangle H$, $\triangle S$	58
21.	-do-	Na^+/Ba^{2+}, Mg^{2+}, Ca^{2+} and Sr^{2+}	K, $\triangle G$, $\triangle H$, $\triangle S$	57
22.	Niobium arsenate	H^+/Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+} and Sr^{2+}	K_H^n, $\triangle G$, $\triangle H^\circ$, $\triangle S$ and $\triangle S_{Lx}$	59
23.	Ce(IV) phosphate	Li^+/H^+, Na^+/H^+, K^+/H^+	$\triangle H^\circ$	78

Studies have also been made towards the thermodynamics of anion exchange on inorganic ion exchangers. The reversibility of Br^--NO_3^- exchange on hydrous zirconia was demonstrated by Kraus[79]. The thermodynamics of Cl^--NO_3^-, Cl^--SCN^- and SCN^--NO_3^- exchange on hydrous zirconium oxide was studied by Nancollas & Paterson[80]. The mechanism for ion exchange capacity appears to be highly specific. Ruvarac and Trtanj[81] studied the thermodynamics of Cl^- and SO_4^{2-} from solution and NO_3^- from hydrous zirconia at 25 -90°C. Thermodynamic quantities (ΔG°, ΔH° and ΔS°) can be calculated by evaluating thermodynamic equilibrium constant.

The use of mixed solvent systems like methanolic water changes ΔG° and changes ΔH° and ΔS° of the exchange of Cl^- for NO_3^- in hydrous zirconia[82] and thus the selectivity constant is affected. Selectivity reversal occurs by increasing the concentration of methanol in the mixture above a certain level. Misak and Mikhail[83] studied the thermodynamics of NO_3^-/Cl^-, NO_3^-/Br^- and NO_3^-/SCN^- exchanges in hydrous ceria. Selectivity reversal of monovalent anions do occur in the weak base hydrous oxides like ceria and zirconia. Certain models like Eisenman model may throw some light on the phenomena involved in anion exchange of hydrous oxides but certain factors like non-coulombic electrostatic attractions and oxide entropy changes have been ignored in this model. Dyer and Malik[84]

commented on the thermal and chemical stabilities and selectivities of commercially available inorganic anion exchangers with the help of exchange isotherms for the ions SO_4^{2-}, NO_3^-, Cl^-, Br^- and I^-. Hysteresis loops were obtained in the anion exchange isotherms obtained for the exchange of NO_3^-/Cl^-, NO_3^-/SCN^-, SO_4^{2-}/Cl^- and SO_4^{2-}/SCN^- on hydrous thorium oxide[85].

Although thermodynamics is a powerful tool for investigating the conditions at equilibrium. However, it is interested only in the initial and final states of a system and it does not consider about the mechanism of the change of one state to the other and the time required thereon. Kinetics takes these factors into consideration.

The kinetics of simple homogeneous chemical reactions is governed by the rate of the reaction depending upon the concentrations of the reactants

$$xA + yB \longrightarrow \text{Product}$$

$$R = k.[A]^x.[B]^y$$

where k is the rate constant, [A] and [B] are the concentration of reacting species and x and y are orders of the reaction with respect to A and B respectively.

Ion-exchange, however, is somewhat different from such chemical reactions. In the first case ion-exchange involves the transport of ions from solution into exchanger phase and vice-versa. Ion-exchangers constitute a different phase than the solution phase and hence the process is heterogeneous. Secondly, in ion-exchange process colons have no part to play in the overall reaction mechanisms, only the counter ions are responsible for this process. Electroneutrality in each phase and at all times is to be maintained. Thus the number of charges carried by the counter ions of one type into the exchanger phase must be equal to the number of charges carried by the other type of counter ions leaving the exchanger phase into the solution phase, at the same time. This coupling of flows of the entering and leaving ions simplifies the treatment of ion-exchange kinetics.

Ion-exchange process thus can be considered as made up of following steps:

1. Migration of counter ion A from ion-exchanger particle into the film adhered to the particle.
2. Migration of counter ion A from the film into the solution.
3. Migration of counter ion B from the solution into the film.
4. Migration of counter ion B from the film into the particle.

Since the rate is determined by the slowest step, it is important to consider all these steps.

Three distinct types of kinetic processes may be considered in an ion-exchange process:

(1) Inter-diffusion of counter ions in the adherent film, the film diffusion control.

(2) Inter-diffusion of counter ions in the ion exchanger itself, the particle diffusion control.

(3) Chemical exchange reaction between the two types of counter ions.

It is an important point to note that of all the exchange kinetics which have appeared in the literature to date, none has been shown to be controlled by the chemical exchange reaction. However, it is not surprising when strong acid and strong base exchangers are used where the common counter ions do not form the chemical bond with the fixed ionogenic group but is somewhat remarkable when there is a complex formation. Even in such cases the kinetically slow step was found to be particle diffusion and not chemical exchange reaction. Furthermore the rate determining step also depends upon experimental conditions. Some theoretical and practical approaches can be applied to decide the mechanism of ion-exchange rate.

Nachod and Wood[86] have made the first serious attempt on the kinetic studies of ion-exchange. They have studied the reaction rate with which ions from solutions are removed by the solid ion-exchanger or conversely the rate with which the

exchangeable ions are released from the exchanger. Boyd et al.[87] have later on studied kinetics of metal ions upon the resin beads and have given a clear understanding about the particle and film diffusion phenomena which govern the ion-exchange. Reichenberg[88] confirmed that at high concentrations the rate is independent of ingoing ion (particle diffusion), while at low concentration the reverse is true (film diffusion). Nancollas[89] studied the kinetics of Na^+-R^+ exchange on crystalline zirconium phosphate. The rate of exchange is initially fast and then becomes slow, suggesting a change in crystal structure. Fuge and Kikindi[90] studied the kinetics of ion-exchange between alkali metals and zirconium antimonate in H^+ form at 25°C. They found that the rate of the reaction increases with the atomic number of the cation. Alberti et al.[91] have observed that the rate of exchange decreases from Ba^{2+} to Sr^{2+} and that it is particularly low for Mg^{2+} ion. Since the energy of hydration of given M^{2+} ion decreases with its crystalline radius, it is likely that the lower exchange rate of Mg^{2+} is related to its relatively larger hydration energy. Therefore, it is difficult for the large hydrated Mg^{2+} to diffuse in the reticular structure of zirconium phosphate phases having low interlayer distances.

Costantino et al.[92] have studied the self diffusion of Na^+ and K^+ ions on microcrystals of $Zr(NaPO_4)_2.3H_2O$ and $Zr(KPO_4).3H_2O$ and modified the Fick's equation to take into

account the non-uniformality of the particle size. The equation obtained have been employed in a study of self diffusion rate of Na^+ and K^+ ions in the above exchanger.

Recently kinetic studies on inorganic ion exchangers were made in our laboratories. A kinetic study of exchange of cations Ag^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Y^{3+} and Th^{4+} was made on tantalum arsenate[93]. The mechanism was controlled by particle diffusion. The kinetics of exchange reactions of Ag^+, Zn^{2+}, Cd^{2+}, Hg^{2+}, La^{3+} and Th^{4+} ions on iron(III) antimonate has been studied at different temperatures[94]. The mechanism of cation exchange has been the particle diffusion control which is confirmed by certain plots. Kinetic parameters have been evaluated. Similar studies on stannic arsenate for Na^+, Zn^{2+}, Mg^{2+}, Cd^{2+}, Ca^{2+} and Al^{3+} have also been made[95]. The application of such studies on clays was also made by studying kinetics of Zn^{2+} exchange on 'Sodium Dickite'[96]. The mechanism has been found to be a film diffusion control. Kinetic parameters has also been evaluated.

The distribution of an ion between the exchanger and solution phases is a measurement of selectivity. Often, the ion-exchanger takes up certain ions in preference to the other present counter ions. This selectivity may depend, mainly upon: (i) Donnan potential, (ii) sieve action, and (iii) complex formation. The selectivity is an important factor to study the

separations. On the basis of distribution coefficients it is possible to predict the separation of one ion from the other. The distribution coefficient is of value as a practical guide to the separation procedures in chromatography. The distribution coefficient for an ion A^+ is given by

$$Kd = \frac{\text{Amount of cation } (A^+) \text{ present in exchanger phase } g^{-1}}{\text{Amount of cation } (A^+) \text{ present in solution phase } ml^{-1}} \quad \ldots\ldots \quad (4)$$

The general use of distribution coeffient is made in elution techniques used in separations. The rate at which ions move in ion-exchange chromatography is proportional to their distribution coefficient.

Analytical ion exchange experiments are best carried out to set the conditions in which the solutions are dilute, loading is low, (say less than 5-10% of total ion exchange capacity) and Kd is thereby nearly constant. The inorganic ion-exchangers have found numerous important analytical applications as categorized below:

(i) Purification of substances on a large scale,

(ii) Separation of one ion from the other on a small ion-exchanger column,

(iii) Ion-exchange paper chromatographic separations,

(iv) Electrophoresis,

(v) Ion-exchanger for gas chromatography,

(vi) Solid state separations,

(vii) Specific spot tests,

(viii) Use of ion-exchanger beads to locate the end point in titration, and

(ix) Use of ion selective electrodes.

Purification on a large scale can be made by passing the sample solution through the ion-exchanger beds which take up certain materials in preference of others. The exchanger bed can be regenerated into suitable form by conventional methods. The technique can also be utilized to recover traces of elements from the dilute solutions. The elements present in ionic form are exchanged by equivalent amount of the counter ion present in the exchanger. The elements can be eluted from the exchanger by suitable electrolytic reagent.

Ion-exchange is, with very few exceptions, a reversible process. The metallic ions are exchanged stoichiometrically with hydrogen ions in exchanger phase and the metal ions can be determined indirectly by the application of exchange reactions:

$$nRH^{+} + M^{n+} \rightleftharpoons MR_n + nH^{+}$$

where R represents the structural unit of the ion-exchanger, and H^{+} and M^{n+} are the cations taking part in the ion-exchange. A

similar method can be adopted for the replacement of anions by hydroxyl ions stoichiometrically.

Ion-exchange has resolved the most difficult problem in chemical analysis i.e. separation of typical components having similar enough properties. Column chromatography is valuable, since the substances separated are collected quantitatively.

Since the crystalline ion-exchangers have cavities of definite size, they also possess ion sieve properties. The counter ions having larger radii than the holes in the cavity can not penetrate and therefore, they can be separated from those smaller ions which can easily enter into the cavity. These separations were first achieved by Clearfield on zirconium phosphate crystals and are summarized below:

Zirconium phosphate and anhydrous metal salt were heated in a platinum dish. The exchange reaction taking place is represented by the following equations:

$$Zr(HPO_4)_2.H_2O + 2/X\ MCl_X \longrightarrow Zr(M)_{2/X}(PO_4)_2 + 2HCl + H_2O$$

When zinc chloride or hafnium chloride were exchanged a new phase was obtained which persisted to about 2/3 of total capacity of exchanger. These wide ranges of metal content forming the same structure indicate that solid solutions of cation within crystal lattice are forming. The fact that a variety of cation type

gives the same phases (almost identical interplaner spacing but different intensities) indicates that the crystal lattice remains rigid with the cations occupying similar exchange sites. This is unlike the behaviour of zirconium phosphate exchanging ions in aqueous electrolyte solution where the lattice expands by the movement of the α-zirconium phosphate layers to accommodate hydrated cations. The elution of cations with dilute acid solutions proved the phenomenon as ion-exchange, the cations could also be removed by contacting the exchange phases with gaseous hydrogen chloride.

Some ion-exchange seperations were also achieved. A solution containing equal parts of lithium chloride and caesium chloride was evaporated to dryness and the dry salt mixture was ground together with α-zirconium phosphate. On heating the mixture at 125°C lithium exchanged leaving caesium because the cavities are large enough to permit a cation of about 2-6° A. Thus Cs^+ should be excluded as was observed experimentally.

However, very few literature is available on ion-exchange in molten salt. Alberti and Allulli treated ion-exchange on amorphous zirconium phosphate in molten nitrates. They found that lithium ion is greatly preferred over potassium ions by the exchanger.

Alberti also studied the specific conductance of amorphous zirconium phosphate in Li^+, Na^+, K^+ and Cs^+ forms

over the range 2-40% conversions. The specific conductance of Li^+ and Cs^+ forms was found to decrease with percent conversion while that of the Na^+ and K^+ forms first increases and then decreases as conversion proceeds. A tentative model was proposed to explain the observed phenomenon.

The preparation of an anion exchange resin with good chemical and thermal stability remains an outstanding problem. The anion exchange resins are usually prepared by introducing an amine or ammonium grouping as a source of positive ionogenic group into polystyrenedivenyl benzene copolymer through a Friedel-Crafts condensation. The common ion exchangers are based on triethylamine. An inorganic anion exchanger can be prepared by introducing triethylamine group into the hydrous oxide of a trivalent or tetravalent metal ions. The amino group may also act as a chelating group to certain cations and hence such a material may be useful in two ways (i) as anion exchange, and (ii) a chelating exchanger.

A new chelating material, titanium(IV) diethanolamine, has been prepared by codification of hydrous titanium oxide[97].

A new class of ion exchange resins was developed by Gregor in 1952 by substituting a chelate group in a highly crosslinked hydrocarbon matrix. Since then many substances known as chelating ion exchanger have been described in the literature. In these types of exchangers the use of chemical

reactions can also be considered to play an important role. The chelating ion exchange materials behave alike true ion-exchangers and the functional group is a chelating group which is fixed within the matrix. Formation of a complex with a metal ion is an example of a coordination compound in which the donor of loan pair of electrons is the complex agent and the central metal ion forms a coordinate covalent bond with it. Formation of the complex depends upon the stability constant of the chelate formed.

A large number of processes for the preparation of chelating ion exchangers have been cited in the literature in the recent past. They are based mainly on condensation, polymerization or addition polymerization and introduction of chelating function either during polymerization or attaching after polymerization.

Varied physical forms may thus be obtained with such a wide range of preparations. Further the nature of chemical additions is based on the introduction of wide range of materials. Chelating exchangers thus have desirable properties of high capacity, high selectivity, kinetics and high mechanical strength.

The present work is undertaken to study the ion exchange equilibria of alkali metal ions on ferric antimonate and that of certain anions on a new zirconium triethylamine anion

exchanger. Kinetics for the transition metal ions is done on stannic oxide. A new anion exchanger, ferric triethylamine has been synthesized and the material has been studied for its ion exchange capacity, pH titration, Kd values, chemical and thermal stabilities. Certain important separations of the anions are achieved on the column of the material.

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CHAPTER - II

ION-EXCHANGE EQUILIBRIA OF ALKALI METAL IONS ON FERRIC ANTIMONATE

Equilibria between ion-exchangers and solutions is being studied with great interest. The earlier studies were made on inorganic ion-exchangers. Studies on organic ion-exchange resins were made after it because of late invention of these resins. Inorganic ion-exchangers swell to negligible extent, and, therefore, the thermodynamics of ion-exchange on these materials will be simpler than on their organic counterparts where swelling is quite appreciable. In recent years several theories of ion-exchange equilibria have been developed and tried on a number of inorganic ion-exchangers. The ion-exchange equilibrium studies on amorphous zirconium phosphate of various compositions and properties have been reported by Larsen and Vissers[1] and Ruvarac[2] for alkali metal ions. Some admirable studies of ion-exchange thermodynamics on semi-crystalline and crystalline zirconium phosphate have been made by Amphlett, Alberti, Noncollas and Dyer at different temperatures with various crystallinities of material for Li^+, Na^+, K^+, Cs^+ and Rb^+ [3-9]. M.Abe, Larsen and Cilley performed the studies of ion-exchange equilibrium on antimonic acid, zirconium phosphate[10-13] and cerium phosphate[14] respectively. Baetsle[15] and Ruvarac[16] reported the ion-exchange equilibria for Ca^{2+}, Sr^{2+}, Ce^{3+} and Eu^{3+} with hydrogen ions at a temperature range 5-70°C on zirconyl phosphate. He also studied the effect of temperature on ion-exchange for Ca^{2+}, Sr^{2+}, Ba^{2+} and La^{3+} on polyantimonic

acid at constant ionic strength[17].

This chapter describes the influence of temperature on the ion-exchange equilibrium of Li^+, Na^+, K^+ and Rb^+ with H^+ on ferric antimonate at constant ionic strength within the temperature range from 30 to 60 °C. A simple approach has been applied and the thermodynamic parameters are calculated.

EXPERIMENTAL

Reagents

Ferric nitrate (B.D.H., India) and antimony pentachloride (B.D.H., England) were used. To prepare the solution of antimony pentachloride one litre of hydrochloric acid 4M was prepared in a standard flask. About 800 ml of this solution is taken in a beaker and the ampule of antimony pentachloride and the beaker containing the 4M hydrochloric acid were cooled to about 2°C by putting them in an icebath. Antimony pentachloride from the ampule was added slowly in the ice cooled 4M HCl with regular stirring by a glass rod in a fumming chamber. This was transferred to a one litre standard flask and made upto the mark with 4M HCl. This prepared solution was about 0.8M. To prepare 0.1M antimony pentachloride solution, 125 ml of this solution was taken in a one litre standard flask and made upto the mark with 4M HCl. All other reagents used were of AnalaR grade.

The solutions of ferric nitrate and antimony pentachloride were prepared in demineralized water and 4M hydrochloric acid respectively.

Synthesis of ferric(III) antimonate

Ferric antimonate was synthesized as reported earlier[18]

by mixing 0.1M solutions of iron(III) nitrate and antimony pentachloride. The zero pH of the final solution was adjusted by adding ammonia solution dropwise with constant shaking. The product was allowed to stand for 24 hours. It was filtered, washed with demineralized water and dried in a temperature controlled oven at 40°C. The product brokedown into small particles when immersed in water. The material was converted into H^+ form by treatment with 2M nitric acid for 24 hours with occasional shaking and intermittent changing the acid. All the samples were again dried at 40°C.

Procedure

The equilibrium experiments were performed by shaking 20 ml solution containing hydrochloric acid solution and appropriate alkali metal solutions having constant ionic strength 0.10 in stoppered conical flasks. To this 0.5 gm of exchanger in hydrogen form was added and flasks were shaken thoroughly in a temperature controlled shaker for 6 hours at desired temperatures. Experiments showed that equilibrium was attained within this period and aliquotes from supernatant solutions were analyzed for hydrogen ions concentration by titrating it against standard NaOH solution.

RESULTS

The exchange isotherms for various cations at different temperatures are plotted in Figures 1 to 4.

The results of ionic fractions of metal ions, selectivity coefficients and thermodynamic equilibrium constants are given in Tables II to V.

TABLE II

IONIC FRACTIONS OF Li^+, SELECTIVITY COEFFICIENTS AND THERMODYNAMIC EQUILIBRIUM CONSTANTS FOR Li^+-H^+ EXCHANGE ON FERRIC ANTIMONATE

X_{Li}	$\bar{X}_{Li}$	K_C	K_a
	(a) Li^+-H^+ at 30 ± 1°C		
0.0014	0.0016	0.5028	
0.0932	0.0282	0.4927	
0.1932	0.0483	0.4254	
0.2862	0.0984	0.3642	
0.3769	0.1250	0.3266	
0.4728	0.1983	0.2590	0.0769
0.5605	0.2816	0.1654	
0.6559	0.3150	0.1568	
0.7489	0.3630	0.1291	
0.8419	0.4150	0.1047	
0.9302	0.4983	0.0745	

(Table II continued)

X_{Li}	$\bar{X}_{Li}$	K_c	K_a
	(b) Li^+-H^+ at 40 ± 1°C		
0.0030	0.0017	0.5028	
0.0955	0.0216	0.4927	
0.1911	0.0317	0.4142	
0.2600	0.0617	0.3599	
0.3793	0.1183	0.3049	0.0634
0.4746	0.1817	0.2514	
0.6029	0.2650	0.1605	
0.6582	0.2983	0.1482	
0.7512	0.3483	0.1151	
0.8442	0.3983	0.0921	
0.9325	0.4816	0.0672	
	(a) Li^+-H^+ at 50 ± 1°C		
0.0020	0.0010	0.5048	
0.0979	0.0150	0.4889	
0.1978	0.0151	0.4126	
0.2908	0.0651	0.3478	
0.3814	0.1117	0.3012	0.0499
0.4768	0.1652	0.2476	
0.6052	0.2483	0.1535	
0.6605	0.2817	0.1416	
0.7535	0.3317	0.1088	
0.8465	0.3817	0.0904	
0.9349	0.4650	0.0605	

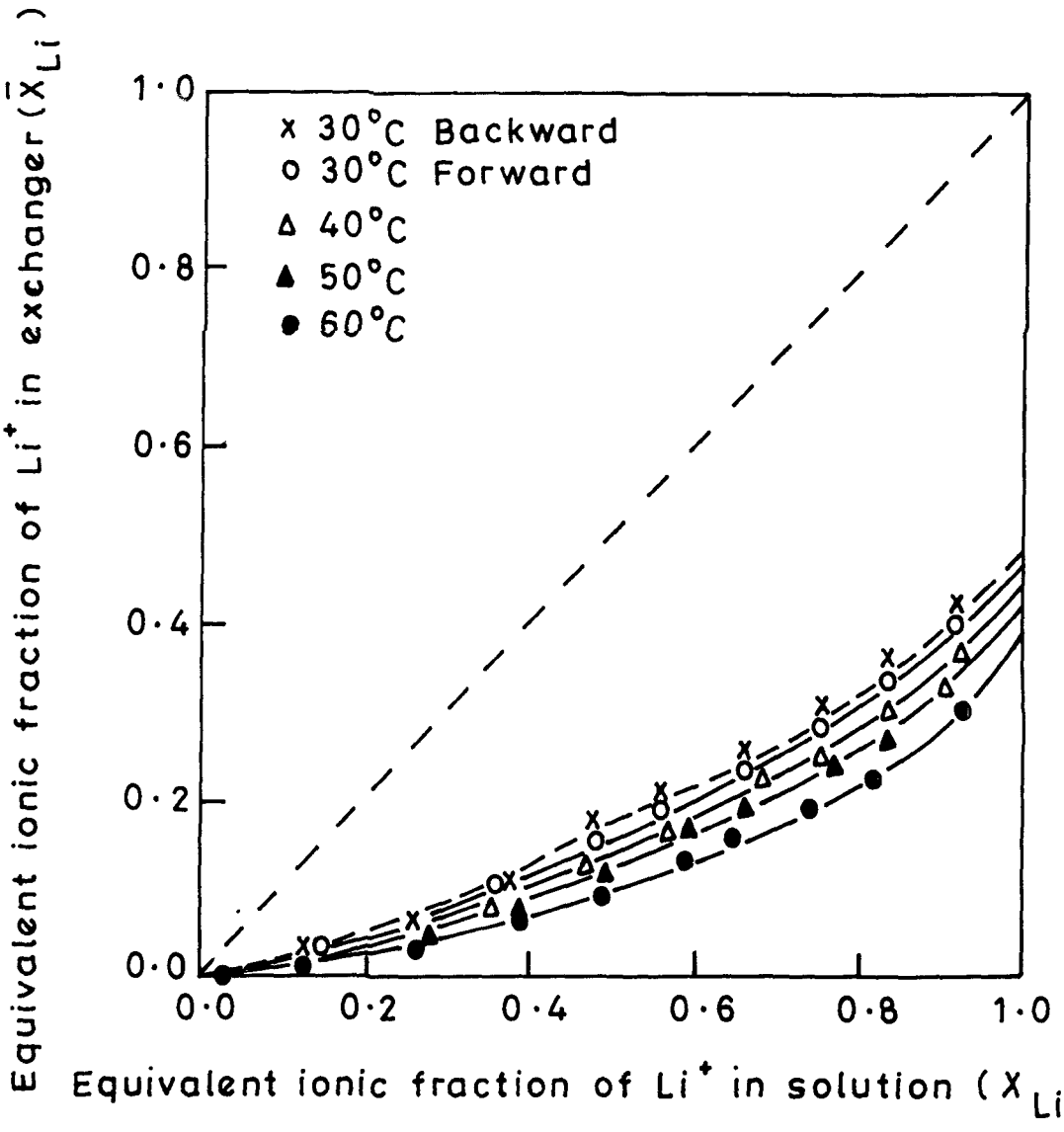

FIG.1 ION EXCHANGE ISOTHERM OF $Li^+ - H^+$ EXCHANGE ON IRON(III) ANTIMONATE

(Table II continued)

X_{Li}	$\bar{X}_{Li}$	K_C	K_B
	(d) Li^+-P^+ at 60 ± 1°C		
0.0020	0.0010	0.5048	
0.0979	0.0150	0.4884	
0.1978	0.0151	0.4112	
0.2817	0.0650	0.3447	
0.3815	0.1089	0.2971	
0.4792	0.1485	0.2432	0.0419
0.6075	0.2317	0.1502	
0.6628	0.2651	0.1384	
0.7558	0.3151	0.1016	
0.9498	0.3650	0.0872	
0.9372	0.4483	0.0544	

TABLE III

IONIC FRACTIONS OF Na^+, SELECTIVITY COEFFICIENTS AND THERMODYNAMIC EQUILIBRIUM CONSTANTS FOR Na^+-H^+ EXCHANGE ON FERRIC ANTIMONATE

X_{Na}	$\bar{X}_{Na}$	K_C	K_o
	(a) Na^+-H^+ at 30 ± 1 °C		
0.0031	0.0013	0.7718	
0.0900	0.0869	0.7622	
0.1455	0.1256	0.6307	
0.3174	0.1521	0.5149	
0.3766	0.2036	0.3857	
0.4744	0.2219	0.3159	0.0480
0.5720	0.2606	0.2649	
0.6678	0.2995	0.1929	
0.7656	0.3484	0.1302	
0.8567	0.3700	0.0982	
0.9249	0.4528	0.0726	
	(b) Na^+-H^+ at 40 ± 1 °C		
0.0031	0.0013	0.7718	
0.0922	0.0869	0.7394	
0.1979	0.1252	0.5625	
0.2833	0.1518	0.4684	
0.3789	0.2024	0.3055	
0.4767	0.2204	0.2568	0.0354
0.5723	0.2573	0.2316	
0.6700	0.2950	0.1647	
0.7656	0.3451	0.1235	
0.8567	0.3668	0.0936	
0.9249	0.4492	0.0686	

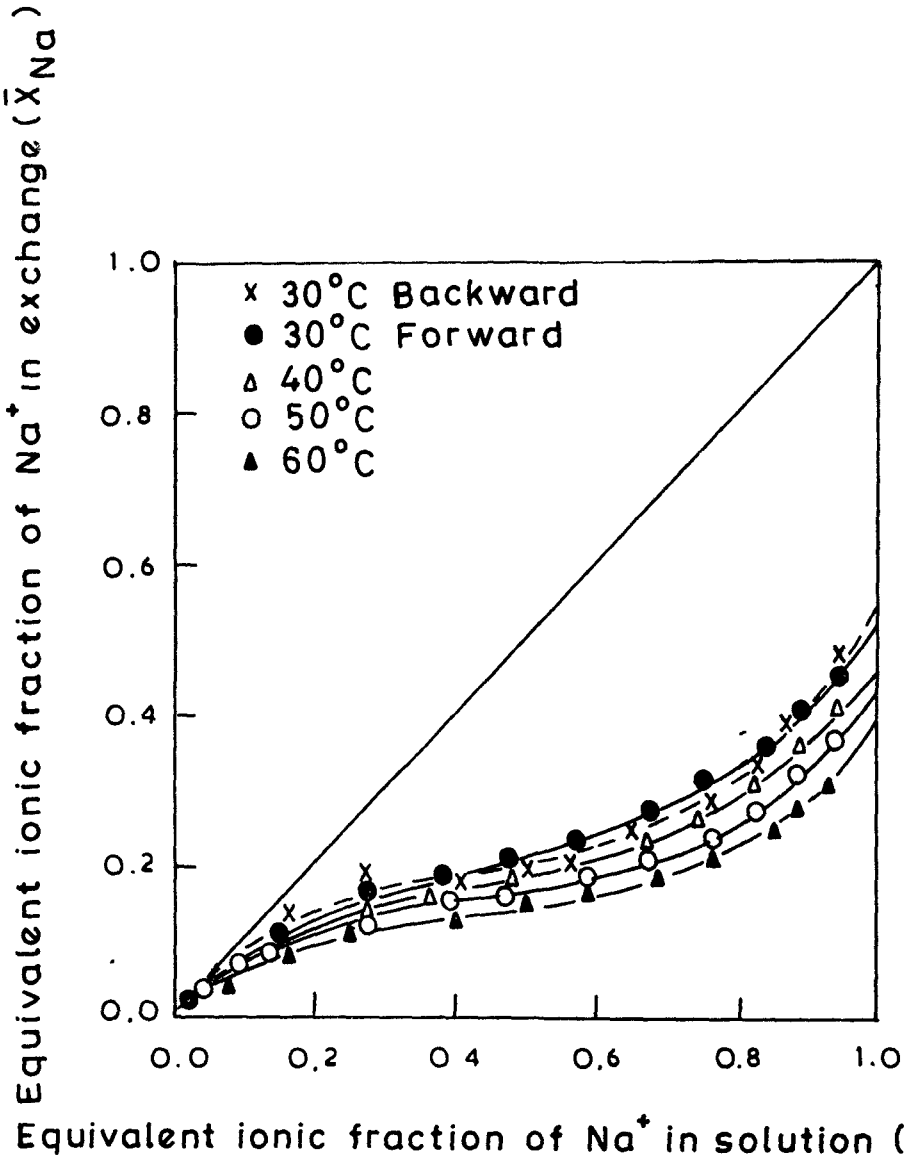

FIG. 2 ION EXCHANGE ISOTHERM OF $Na^+ - H^+$ EXCHANGE ON IRON (III) ANTIMONATE

(Table III continued)

X_{Na}	$\bar{X}_{Na}$	K_C	K_a
	(c) Na^+–H^+ at 50 ± 1°C		
0.0031	0.0013	0.7701	
0.0891	0.0858	0.7155	
0.1905	0.1240	0.5319	
0.2758	0.1510	0.4263	
0.3812	0.2011	0.2669	
0.4790	0.2186	0.2363	0.0314
0.5745	0.2555	0.1879	
0.6724	0.2938	0.1353	
0.7357	0.3414	0.0914	
0.8612	0.3512	0.0938	
0.9249	0.4249	0.0507	
	(d) Na^+–H^+ at 60 ± 1°C		
0.0031	0.0013	0.7701	
0.0343	0.0676	0.7196	
0.1375	0.1163	0.5350	
0.2451	0.1452	0.3802	
0.3647	0.1836	0.2941	
0.4813	0.2026	0.2443	0.0217
0.5745	0.2410	0.1465	
0.6746	0.2802	0.1101	
0.7702	0.3389	0.0751	
0.8635	0.3473	0.0690	
0.9249	0.4249	0.0382	

TABLE IV

IONIC FRACTIONS OF K^+, SELECTIVITY COEFFICIENTS AND THERMODYNAMIC EQUILIBRIUM CONSTANTS FOR K^+-H^+ EXCHANGE ON FERRIC ANTIMONATE

X_K	$\bar{X}_K$	K_C	K_a
	(a) K^+-H^+ at 30 ± 1°C		
0.0042	0.0074	3.9242	
0.0695	0.1270	3.7133	
0.1582	0.2192	2.2609	
0.2512	0.2667	1.5907	
0.3516	0.3455	0.9732	
0.3989	0.3610	0.8513	0.3646
0.4854	0.4091	0.7359	
0.6360	0.4571	0.3511	
0.7315	0.4809	0.3274	
0.8225	0.5532	0.2671	
0.9112	0.6357	0.1685	
	(b) K^+-H^+ at 40 ± 1°C		
0.0042	0.0072	3.8017	
0.0695	0.1270	3.7083	
0.1605	0.1996	2.0533	
0.2539	0.2500	1.4481	
0.3670	0.3292	0.8464	
0.4517	0.3448	0.6387	0.3005
0.4954	0.4093	0.7162	
0.6582	0.4408	0.3468	
0.7338	0.4726	0.3050	
0.8248	0.5369	0.2462	
0.9135	0.6175	0.1528	

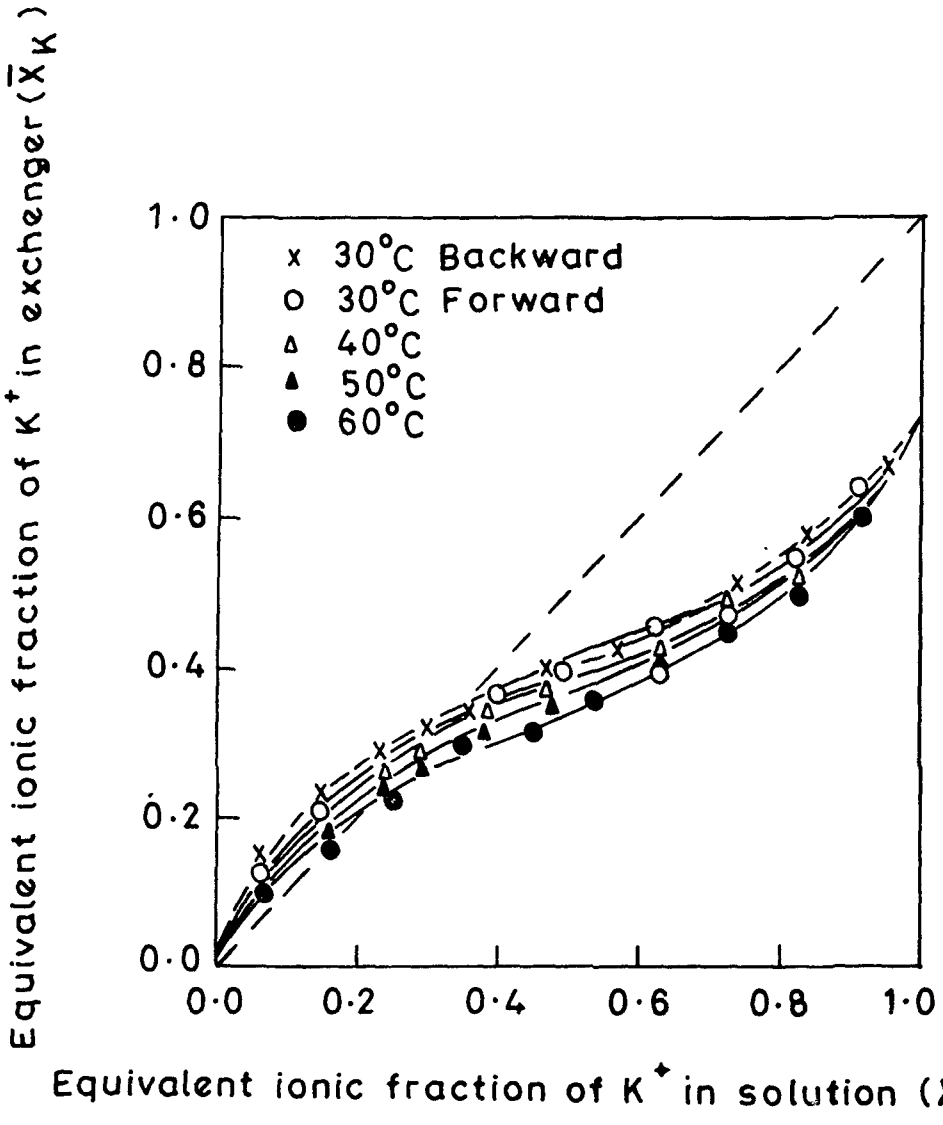

FIG.3 ION EXCHANGE ISOTHERM OF $K^+ - H^+$ EXCHANGE ON IRON (III) ANTIMONATE

(Table IV continued)

X_K	$\bar{X}_K$	K_C	K_a
	(c) K^+-H^+ at 50 ± 1 °C		
0.0044	0.0069	3.7514	
0.0718	0.1114	3.7235	
0.1605	0.1619	2.0533	
0.2538	0.2431	1.4481	
0.3561	0.3130	0.8238	
0.4562	0.3423	0.7307	0.2687
0.5472	0.3766	0.4998	
0.6405	0.4246	0.3085	
0.7383	0.4401	0.2786	
0.8271	0.5207	0.2270	
0.9135	0.6175	0.1328	
	(d) K^+-H^+ at 60 ± 1 °C		
0.0044	0.0068	3.7514	
0.0718	0.1114	3.7235	
0.1605	0.1619	2.0533	
0.2538	0.2184	1.4481	
0.3561	0.3019	0.8238	
0.4561	0.3123	0.7307	0.2228
0.5495	0.3603	0.4616	
0.6248	0.4083	0.4228	
0.7406	0.4739	0.2577	
0.8370	0.5044	0.1982	
0.9148	0.6012	0.1286	

TABLE V

IONIC FRACTIONS OF Rb^+, SELECTIVITY COEFFICIENTS AND THERMODYNAMIC EQUILIBRIUM CONSTANTS FOR Rb^+–H^+ EXCHANGE ON FERRIC ANTIMONATE

X_{Rb}	$\bar{X}_{Rb}$	K_c	K_a
	(a) Rb^+–H^+ at 30 ± 1 °C		
0.0072	0.0066	2.1962	
0.0830	0.1562	2.0451	
0.1750	0.2590	1.5714	
0.2695	0.2837	1.2758	
0.3231	0.3765	1.1622	
0.4567	0.4325	0.9066	0.5970
0.5556	0.4437	0.6379	
0.6481	0.5187	0.5851	
0.7427	0.5725	0.4639	
0.8352	0.6474	0.3622	
0.9277	0.7225	0.2738	
	(b) Rb^+–H^+ at 40 ± 1 °C		
0.0073	0.0066	2.1906	
0.0832	0.1471	2.0451	
0.1753	0.2241	1.4414	
0.2738	0.2687	1.2513	
0.3642	0.3362	0.9377	
0.4610	0.3986	0.8261	0.5141
0.5599	0.4012	0.5268	
0.6502	0.4762	0.5326	
0.6876	0.5380	0.4579	
0.8352	0.6262	0.3418	
0.9277	0.7012	0.2529	

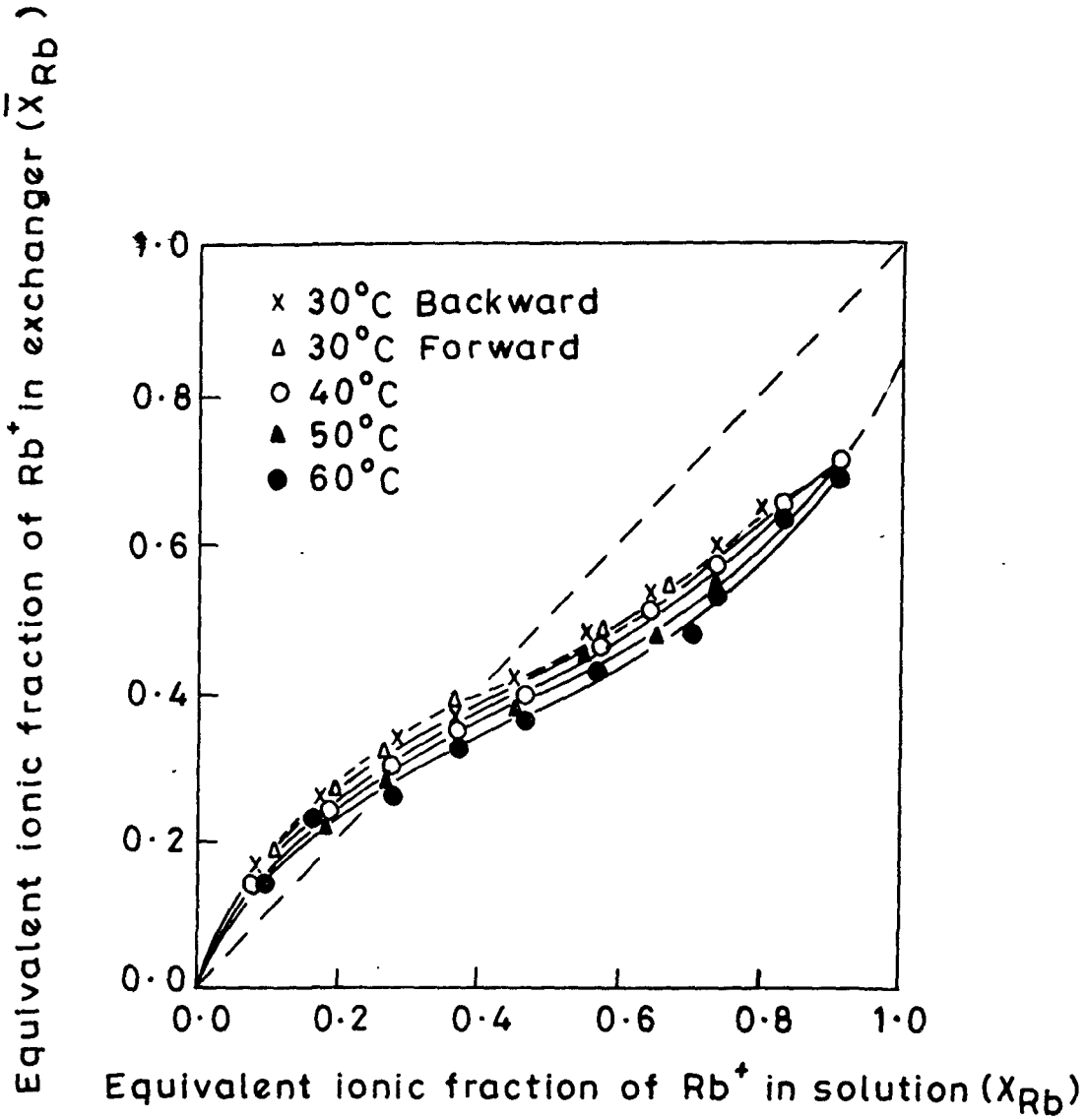

FIG. 4 ION EXCHANGE ISOTHERM OF $Rb^+ - H^+$ EXCHANGE ON IRON (III) ANTIMONATE

(Table V continued)

X_{Rb}	$\bar{X}_{Rb}$	K_c	K_a
	(c) Rb^+-H^+ at 50 ± 1°C		
0.0073	0.0066	2.1906	
0.0830	0.1471	2.0451	
0.1771	0.2241	1.3803	
0.2760	0.2687	1.2014	
0.3663	0.3362	0.8762	
0.4631	0.3615	0.7475	0.4481
0.5598	0.4587	0.5269	
0.6523	0.4698	0.4845	
0.7470	0.5380	0.3076	
0.8373	0.6130	0.3255	
0.9298	0.6941	0.2370	
	(d) Rb^+-H^+ at 60 ± 1°C		
0.0073	0.0066	2.1906	
0.0830	0.1471	1.9441	
0.1771	0.2174	1.4580	
0.2760	0.2687	1.1576	
0.3665	0.3267	0.8322	
0.4652	0.3525	0.7523	0.3991
0.5641	0.4314	0.5154	
0.6545	0.4732	0.4708	
0.7470	0.5289	0.3537	
0.8373	0.6250	0.2399	
0.9298	0.6942	0.2075	

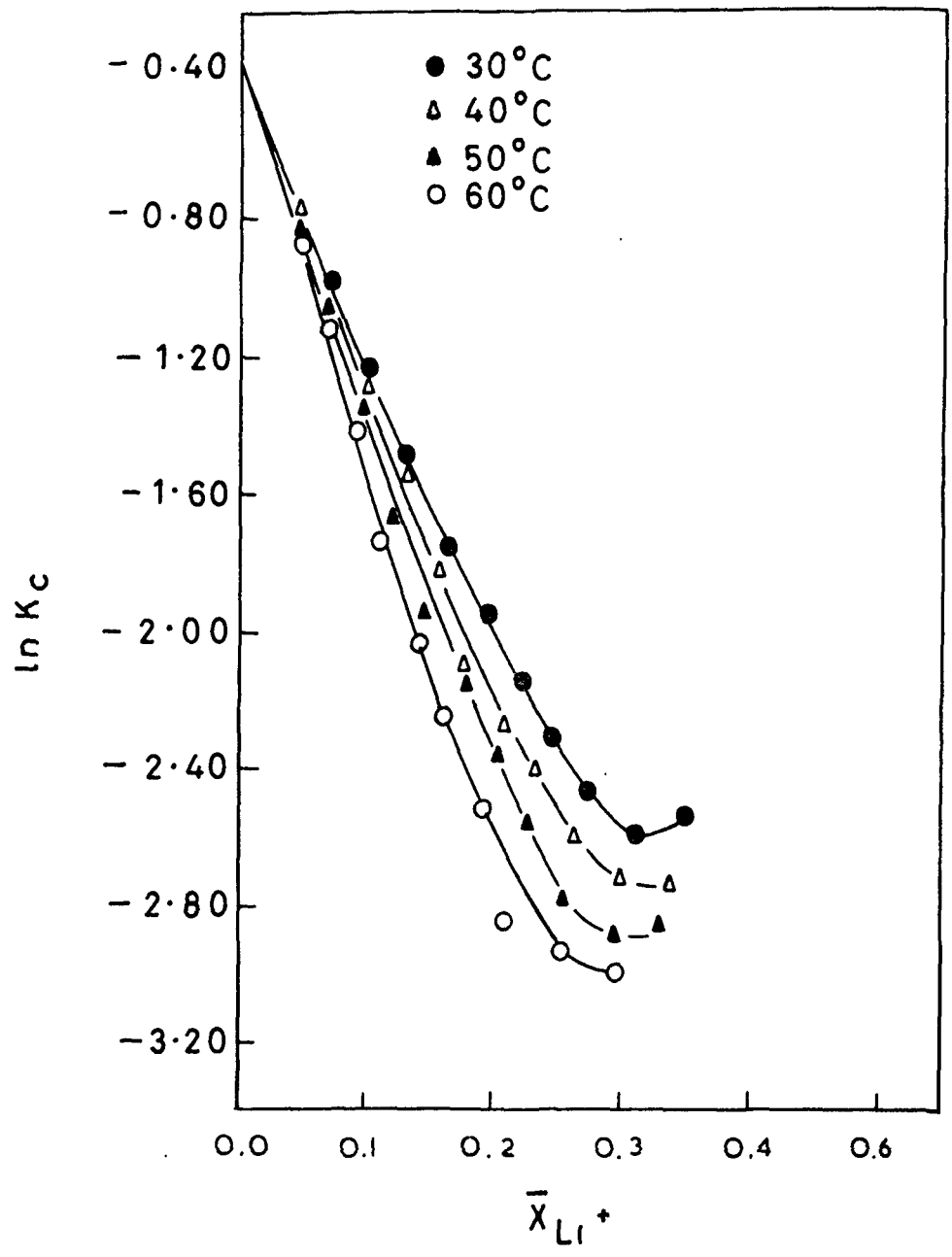

FIG.5 ln OF SELECTIVITY COEFFICIENTS VS. IONIC FRACTIONS OF Li^+ IN EXCHANGER PHASE

The plots of ln K_c vs. ionic fraction of cation in exchanger phase are presented in Figures 5 to 8. The thermodynamic equilibrium constants calculated from these plots are given in Tables II to V.

The values of enthalpy change $\triangle H^\circ$, free energy change, $\triangle G^\circ$ and entropy change $\triangle S^\circ$, were calculated. Results of these thermodynamic parameters are given in Tables VI to IX.

TABLE VI

THERMODYNAMIC PARAMETERS FOR Li^+-H^+ EXCHANGE ON FERRIC ANTIMONATE AT CONSTANT IONIC STRENGTH AT VARIOUS TEMPERATURES

Thermodynamic parameters	30 ± 1 °C	40 ± 1 °C	50 ± 1 °C	60 ± 1 °C
K_a	0.08	0.06	0.05	0.04
$\triangle G^\circ$ (KJ/mole)	6.50	7.20	8.10	8.78
$\triangle H^\circ$ (KJ/mole)		17.06		
$\triangle S^\circ$ (J/mole/degree)	77.62	77.43	77.73	77.60

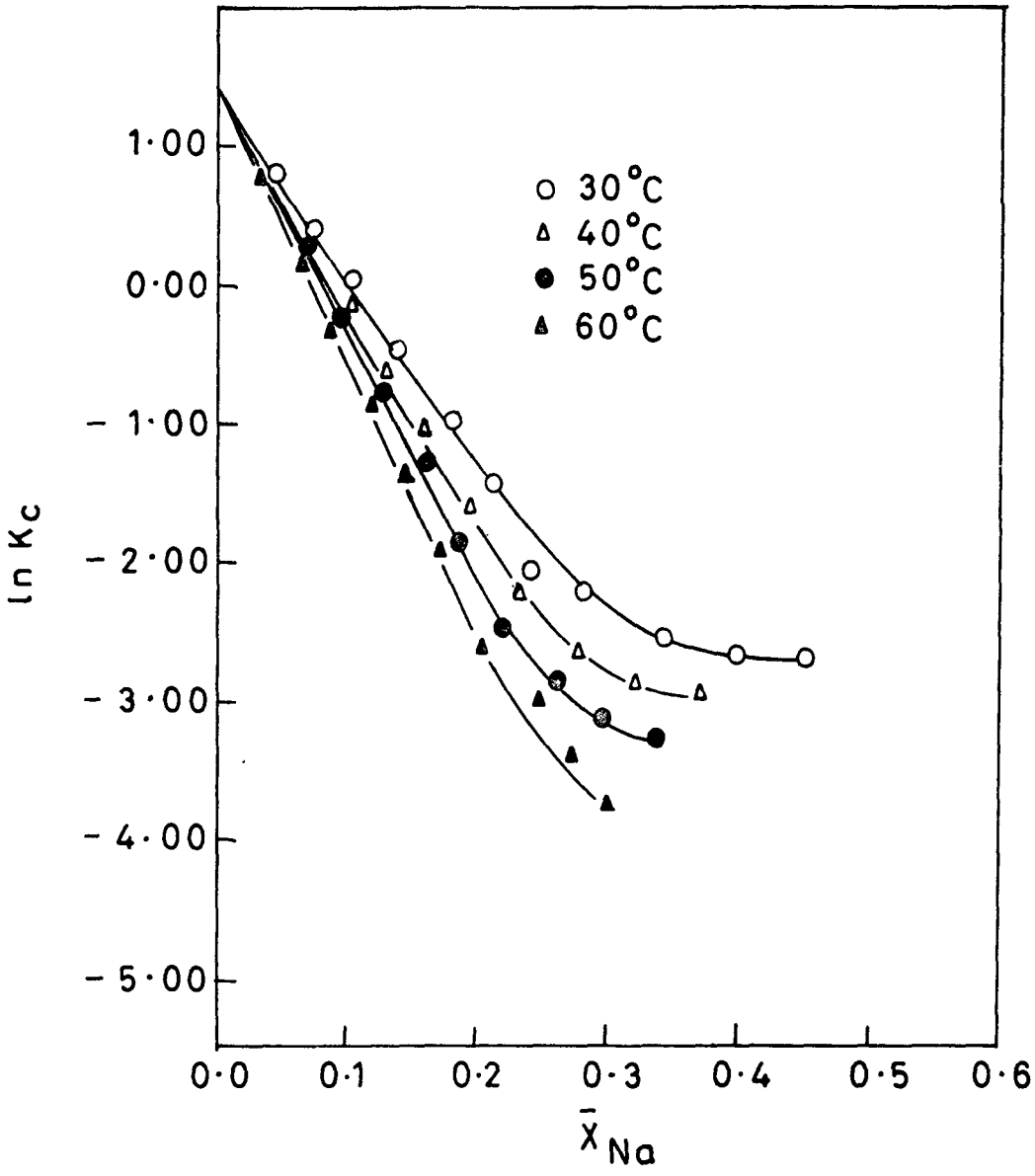

FIG. 6 ln OF SELECTIVITY COEFFICIENTS VS. IONIC FRACTIONS OF Na^+ IN EXCHANGER

TABLE VII

THERMODYNAMIC PARAMETERS FOR Na^+-H^+ EXCHANGE ON FERRIC ANTIMONATE AT CONSTANT IONIC STRENGTH AT VARIOUS TEMPERATURES

Thermodynamic parameters	30 ± 1 °C	40 ± 1 °C	50 ± 1 °C	60 ± 1 °C
K_a	0.05	0.04	0.03	0.02
$\triangle G^\circ$ (KJ/mole)	7.69	8.74	9.61	10.66
$\triangle H^\circ$ (KJ/mole)		22.17		
$\triangle S^\circ$ (J/mole/degree)	98.55	98.76	98.40	98.58

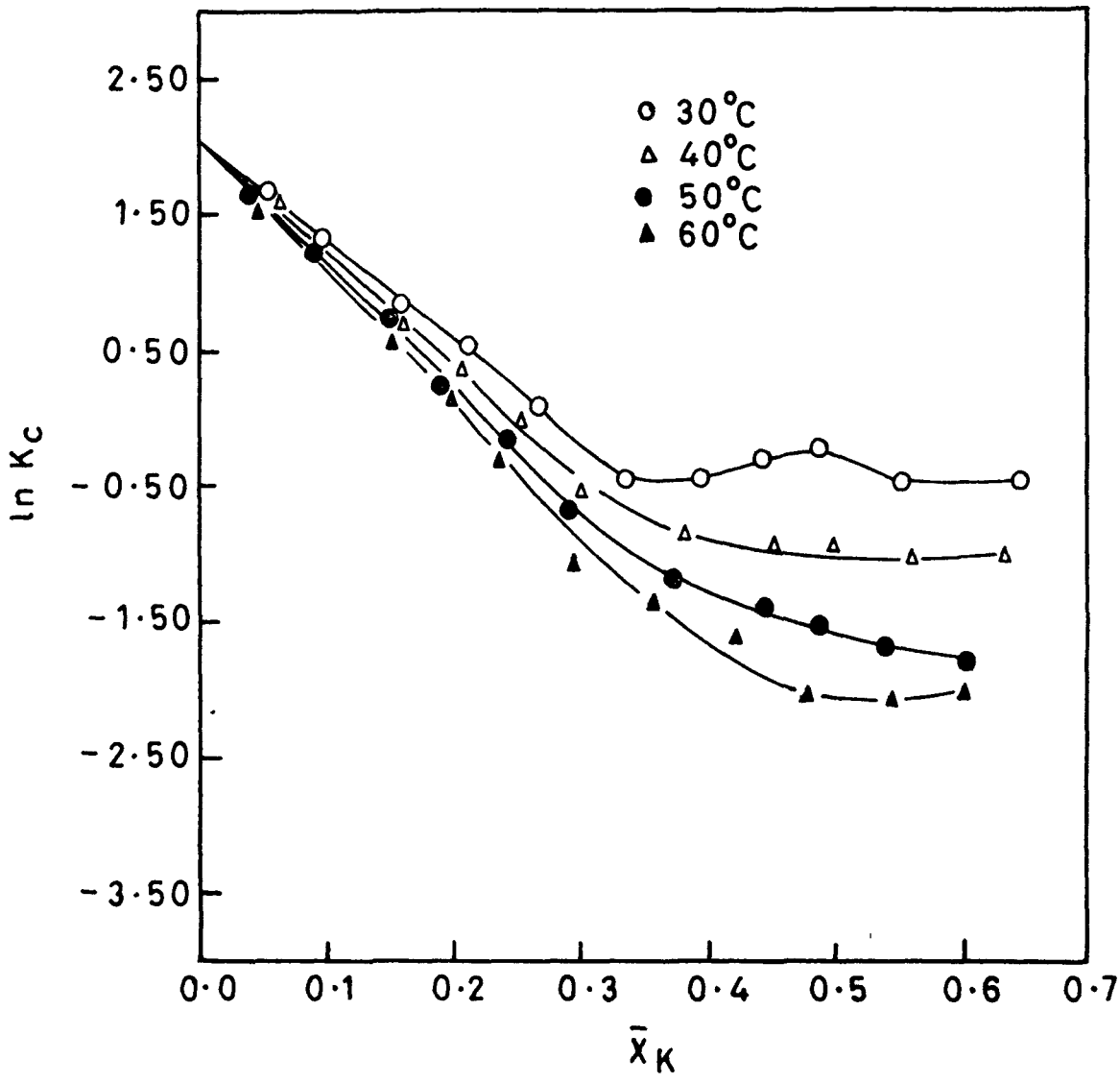

FIG.7 In OF SELECTIVITY COEFFICIENTS VS. IONIC FRACTIONS OF K^+ IONS IN THE EXCHANGER PHASE

TABLE VIII

THERMODYNAMIC PARAMETERS FOR K^+-H^+ EXCHANGE ON FERRIC ANTIMONATE AT CONSTANT IONIC STRENGTH AT VARIOUS TEMPERATURES

Thermodynamic parameters	30 ± 1°C	40 ± 1°C	50 ± 1°C	60 ± 1°C
K_a	0.37	0.30	0.27	0.22
$\triangle G^\circ$ (KJ/mole)	2.56	3.15	3.55	4.18
$\triangle H^\circ$ (KJ/mole)		13.85		
$\triangle S^\circ$ (J/mole/degree)	54.14	54.29	53.86	54.14

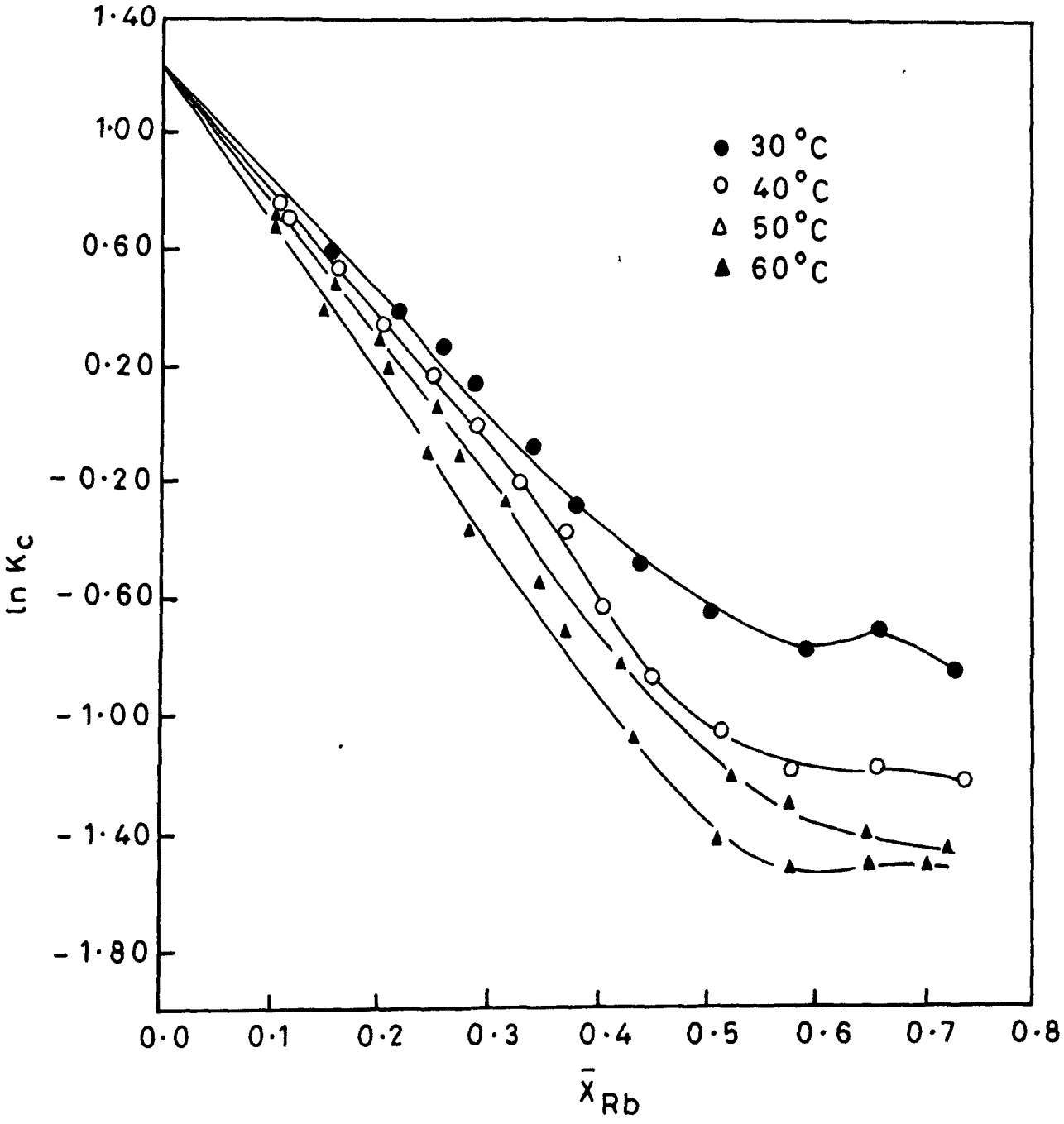

FIG.8. ln OF SELECTIVITY COEFFICIENTS VS. IONIC FRACTIONS OF Rb^+ IN EXCHANGER PHASE

TABLE IX

THERMODYNAMIC PARAMETERS FOR Rb^+-H^+ EXCHANGE ON FIBRIC ANTIMONATE AT CONSTANT IONIC STRENGTH AT VARIOUS TEMPERATURES

Thermodynamic parameters	30 ± 1°C	40 ± 1°C	50 ± 1°C	60 ± 1°C
K_a	0.60	0.51	0.45	0.40
$\triangle G^\circ$ (KJ/mole)	1.31	1.74	2.17	2.56
$\triangle H^\circ$ (KJ/mole)		11.09		
$\triangle S^\circ$ (J/mole/degree)	40.90	40.991	41.033	40.971

DISCUSSION

Ferric antimonate in hydrogen form behaves as a monoprotic weak acid. The exchange with monovalent ions on ferric antimonate can be represented by the following equation:

$$RH^+ + M^+ \rightleftharpoons RM^+ + H^+ \quad \ldots \quad (1)$$

Ion-exchange process, being stoichiometric, will give amount of hydrogen ion liberated equivalent to the metal ion (M^+) taken by the exchanger. Such an exchange is presented in Tables IV to V and plotted in Figures 1 to 4 in the form of ion-exchange isotherms for the forward and backward processes. These results indicate that S shaped curves are obtained for Li^+, Na^+, K^+ and Rb^+ ions with different selectivities and the exchange is reversible in all these cases as the forward process isotherms coincide with the backward process isotherms. The preference of Li^+ and Na^+ is lesser than for H^+ to ferric antimonate. At low concentrations of K^+ the uptake is slightly more than that of H^+ but at high concentrations the uptake of K^+ is lesser than that of H^+. Nearly same trend is observed with Rb^+ except that at low concentrations the relative uptake of Rb^+ is slightly more as compared with that of K^+. This uptake, therefore, follows the trend as: $Na^+ < Li^+ < K^+ < Rb^+$ at low concentrations. For an overall comparison the equilibrium constant will be helpful.

The selectivity coefficient, K_C, for ion-exchange reaction (equation 1) is calculated as follows:

$$K_C = \frac{\bar{X}_M \cdot X_H}{\bar{X}_H \quad X_M} \times \frac{\gamma_H}{\gamma_M} \qquad \ldots \qquad (2)$$

where $\bar{X}_M$ is the equivalent fraction of metal in the exchanger phase, X_H and X_M, the equivalent fraction of hydrogen and metal in the solution phases respectively. γ_H and γ_M the activity coefficients of hydrogen and metal respectively in the solution. For dilute concentrations the ratio $\frac{\gamma_H}{\gamma_M}$ may be taken as unity.

The values of K_C at different concentrations and different temperatures as presented in Tables II to V indicate that K_C decreases with rise in metal ion concentration. K_C also decreases with rise in temperature as well.

The thermodynamic equilibrium constant, K_a is calculated following the expression given by Gaines & Thomas[19]

$$\ln K_a = (Z_A - Z_B) + \int_0^1 \ln K_C \, d\bar{X}_M \qquad \ldots \qquad (3)$$

the thermodynamic equilibrium constant, K_a calculated following the equation (3) (Tables VI to IX) and the Figures 5 to 8 reveal that alkali metals at all the temperatures ranging from 30° to 60°C however, the degree of selectivity decreases

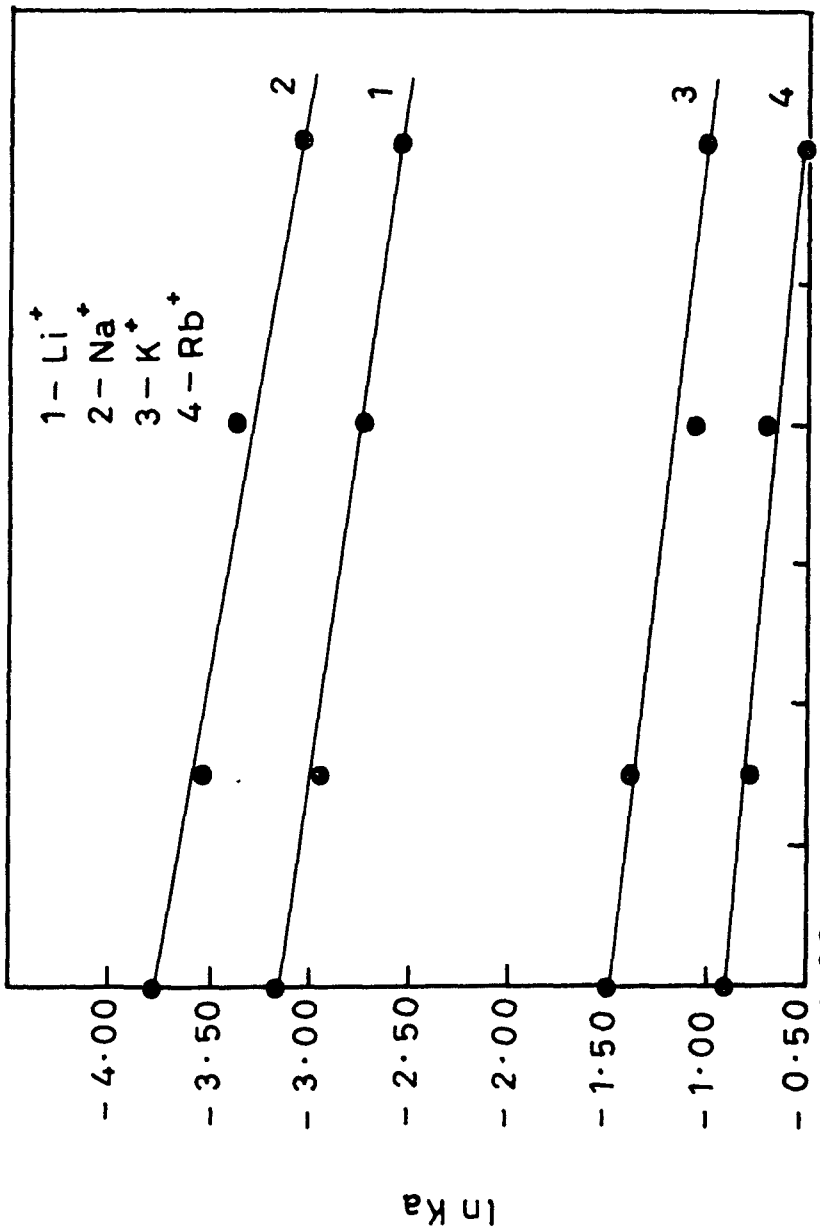

FIG.9 TEMPERATURE DEPENDENCE OF THE THERMODYNAMIC EQUILIBRIUM CONSTANT

as compared to that of at lower temperatures. A comparative study of K_a values at different temperatures for different alkali metal ions reflects the selectivity order of alkali metal ions as $Na^+ < Li^+ < K^+ < Rb^+$.

The standard free energy of exchange, $\triangle G^\circ$ is calculated from the thermodynamic equilibrium constant K_a, using the equation

$$\triangle G^\circ = - \frac{RT}{Z_A Z_B} \ln K_a \qquad \ldots \qquad (4)$$

where R is the gas constant, the Z_A and Z_B are the valencies of competing ionic species. T is the absolute temperature. The results (Tables VI to IX) indicate that during the exchange of alkali metal ions over ferric antimonate in hydrogen form, the free energy change is positive over all the temperatures. At all the temperatures these exchanges are, therefore, nonspontaneous. This is also supported by the view that in H^+ form the ion exchanger behaves as a weak acid which is less ionized as compared to its salt i.e. the tendency to prefer H^+ as compared with alkali metal ions should be effective.

The standard enthalpy change, $\triangle H^\circ$, has been evaluated from the plot of log K_a against $\frac{1}{T}$ (Fig. 9). The results giving (Tables VI to IX) positive enthalpy change indicate that the reaction is endothermic or in other means the binding

energy of one atom of alkali metal is higher than that of one atom of hydrogen.

The standard entropy change, ΔS° is then calculated following the equation

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \quad \ldots \quad (5)$$

The results of entropy change (Tables VI to IX) produce a markable effect on the ion-exchange mechanism. The gain in entropy indicates the lesser order produced in the forward reaction during alkali metal ions transfer to ferric antimonate. The entropy change includes two reactions, one which occurs in the interphase and other in the solution. Ingoing of ions from solution to the solid phase results in a less ordered structure to the alkali metal ions in the matrix which results in the mobilization and increase in the degree of freedom of alkali metal ions in the exchanger phase, which contributes a increase in entropy. Further, the passage of hydrogen ions from solid to solution phase results in lesser ordering of water and a further increase in entropy which are in accordance with the datas on niobium arsenate[20] and ferric antimonate[21].

The hypothetical thermodynamic data in infinitesimal concentration were calculated for interpretation of the selectivity of the alkali metal in the trace amounts on

iron(III) antimonate and for comparison with those data obtained with other exchangers. The values of $(\ln K_c)_{\bar{x}_M \to 0}$ were obtained by extrapolating to zero loading[22] of the alkali metals on Figures 5 to 8. From these values the hypothetical thermodynamic data were calculated by the similar treatment as for the overall equilibrium constant. The accuracy of these values may be higher than those of the latter. The calculated $(\Delta H^\circ)_{\bar{x}_M \to 0}$ values indicate that there is no enthalpy change in the reaction when metal ion concentration in the solid phase approaches to zero over the entire range of temperatures. While the $(\Delta S^\circ)_{\bar{x}_M \to 0}$ increases with increasing ionic radii of alkali metals except for Rb^+. Hypothetical data on "zero loading" of the ion exchange at 30°C are given in Table X.

TABLE X

HYPOTHETICAL THERMODYNAMIC DATA ON "ZERO LOADING" OF THE ION EXCHANGE REACTION AT 30°C

	Li^+	Na^+	K^+	Rb^+
$\ln K_{c\,\bar{x}_M \to 0}$	-0.35	-1.50	-2.00	-1.25
$\Delta G^\circ_{\bar{x}_M \to 0}$/KJ eqvt^{-1}	0.88	3.79	5.06	3.16
$\Delta H^\circ_{\bar{x}_M \to 0}$/KJ eqvt^{-1}	0.00	0.00	0.00	0.00
$\Delta S^\circ_{\bar{x}_M \to 0}$/J eqvt^{-1}	-2.90	-12.50	-16.70	-10.40

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CHAPTER - III

ION EXCHANGE EQUILIBRIA OF $Cr_2O_7^{2-}$, CrO_4^{2-}, $S_2O_3^{2-}$, SO_4^{2-} AND MnO_4^- WITH NO_3^- ON ZIRCONIUM TRIETHYLAMINE

In recent years a number of inorganic ion-exchangers have been synthesized mainly for analytical separations. Besides the development of new materials and their applications, interest has also been developed in the physical chemistry of ion exchange in terms of thermodynamics and kinetics of ion exchange. Thermodynamics deals with the study of ion exchange equilibrium while the kinetics deals with mechanism of exchange. Ion exchange equilibria on cation exchangers have been studied to a larger extent than that of anion exchangers. Only a few thermodynamic studies have been made on inorganic anion exchangers. The equilibrium studies were started with the amphoteric substances like hydrous zirconia[1-4] and hydrous ceria[5]. Emphasis on the selectivity and reversibility of the commercially available inorganic anion exchangers[6] for SO_4^{2-}, NO_3^-, Cl^-, Br^- and I^- has also been given. Thermodynamics of incomplete exchange during sorption of metal complexes by anion exchangers have also been studied[7].

Thermodynamic studies on a new inorganic anion exchanger, zirconium triethylamine are summarized in this chapter, which describes the influence of temperature of the ion exchange equilibria of $Cr_2O_7^{2-}$, CrO_4^{2-}, $S_2O_3^{2-}$, SO_4^{2-} and MnO_4^- with NO_3^- at a constant ionic strength. A simple approach has been applied and the thermodynamic parameters are calculated.

EXPERIMENTAL

Reagents

Zirconium oxichloride (B.D.H.) and triethylamine (E.Merck) were used. All other reagents were of Analar grade.

Synthesis of zirconium triethylamine

It was prepared by mixing 0.1M solution of zirconium oxychloride and triethylamine in the ratio 1:2. Precipitate thus obtained was kept standing for 24 hours at room temperature. Precipitate was filtered and washed with demineralized water and dried at the temperature controlled at 40°C. The dried cold product was immersed in water, the product brokedown into small pieces. The material was converted into nitrate form by keeping in 2 molar sodium nitrate solution for 24 hours and intermittently replacing the supernatent liquid with a fresh solution of sodium nitrate. Sample was washed and dried again at 40°C in the oven. The particles were then sieved to get the products of required size.

Procedure

The material (50-100 mesh) was converted to other anionic forms by placing the material in a column and passing

1.0M potassium or sodium salts of the respective anions until the concentration of anion in the eluent and effluent was identical. The sample was washed with demineralized water until it was free from anions, dried and stored in the stoppered bottle.

Ion exchange capacity

Ion exchange capacities were determined by batch process. 0.5 g of the exchanger was shaken for 24 hours with 50 ml of 2M sodium nitrate solution in the stoppered flasks. Content of the flask was filtered and titrated for different anions.

Equilibrium studies

The equilibrium experiments were performed by taking 20 ml solution containing sodium a potassium nitrate solution and appropriate anion solution. The ionic strength of the total content was kept 0.10 in the stoppered conical flasks. To this 0.2 g of the exchanger in nitrate form was added and flasks were shaken thoroughly in a temperature controlled shaker for 24 hours at desired temperatures. Experiments showed that equilibrium was attained within this period and aliquotes from supernatant solutions were analysed for anions.

Reversibility

For reversibility experiments were performed by equilibrating the exchanger in the particular anionic form with sodium nitrate solution at 30 °C.

RESULTS

The results of the ion exchange capacity for chromate, dichromate, sulphate, thiosulphate and permanganate are presented in Table XI.

TABLE XI

ION EXCHANGE CAPACITY OF SOME ANIONS ON ZIRCONIUM TRIETHYLAMINE

Anion	Salt used	Ion exchange capacity of anionic form of exchanger (meq/g)	Ion exchange capacity of nitrate form of exchanger (meq/g)
$Cr_2O_7^{2-}$	Potassium dichromate	2.00	1.88
CrO_4^{2-}	Potassium chromate	1.62	1.61
SO_4^{2-}	Sodium sulphate	1.14	1.06
$S_2O_3^{2-}$	Sodium thiosulphate	0.56	0.55
MnO_4^-	Potassium permanganate	1.51	1.51

The exchange isotherms for various anions at different temperatures are plotted in Figures 10-14.

The results of equivalent fractions of anions, selectivity coefficients and thermodynamic equilibrium constants are given in Tables XII-XVI.

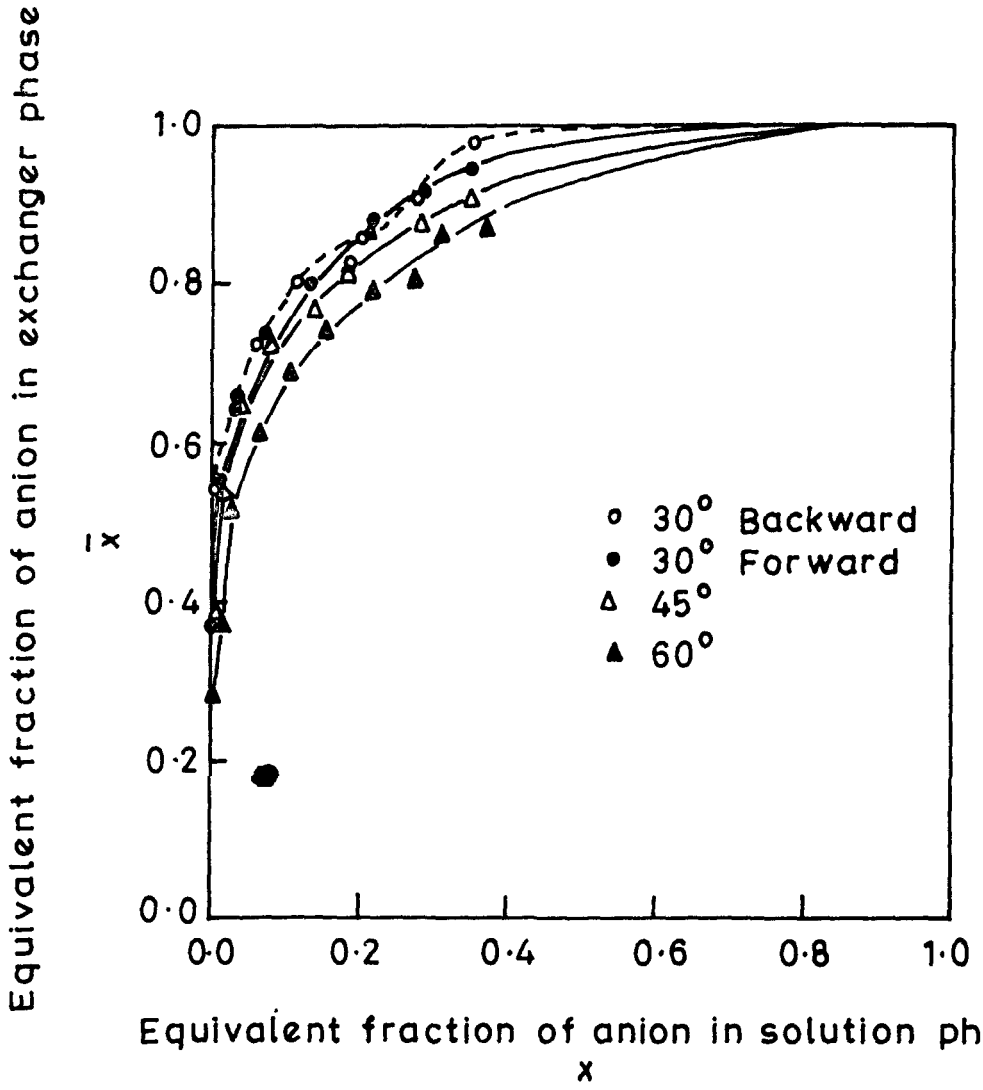

FIG.10 ION EXCHANGE ISOTHERM OF DICHROMATE IONS ON ZIRCONIUM TRIETHYLAMINE

TABLE XII

EQUIVALENT FRACTIONS OF $Cr_2O_7^{2-}$, SELECTIVITY COEFFICIENTS AND THERMODYNAMIC EQUILIBRIUM CONSTANTS FOR $Cr_2O_7^{2-}$-NO_3^- EXCHANGE ON ZIRCONIUM TRIETHYLAMINE

$X_{Cr_2O_7^{2-}}$	$\bar{X}_{Cr_2O_7^{2-}}$	K_c	K_e
	(a) $Cr_2O_7^{2-}$-NO_3^- at 30 ± 1°C		
0.0000	0.1950	326.20	
0.0042	0.3780	230.72	
0.0078	0.5620	158.44	
0.0416	0.6666	132.47	
0.0769	0.7600	146.20	
0.1259	0.8140	159.85	170.28
0.1795	0.8380	119.95	
0.2152	0.8820	181.60	
0.2855	0.9260	259.80	
0.3472	0.9400	320.44	
	(b) $Cr_2O_7^{2-}$-NO_3^- at 45 ± 1°C		
0.0000	0.1950	326.20	
0.0042	0.3780	230.72	
0.0089	0.5517	152.46	
0.0532	0.6584	134.22	
0.0810	0.7560	148.58	
0.1316	0.8016	120.74	64.07
0.1850	0.8322	102.55	
0.2248	0.8775	147.26	
0.2912	0.9100	175.00	
0.3565	0.9246	238.67	

(Table XII continued)

$X_{Cr_2O_7^{2-}}$	$\bar{X}_{Cr_2O_7^{2-}}$	K_c	K_a
	(c) $Cr_2O_7^{2-}$-NO_3^- at 60 ± 1°C		
0.0000	0.1940	326.21	
0.0042	0.3790	230.72	
0.0158	0.5420	142.35	
0.0416	0.6666	132.47	
0.0879	0.7524	150.40	
0.1382	0.7840	90.45	39.25
0.1982	0.8280	97.09	
0.2407	0.8720	128.13	
0.2990	0.8960	136.94	
0.3758	0.9145	219.77	

TABLE XIII

EQUIVALENT FRACTIONS OF CrO_4^{2-}, SELECTIVITY COEFFICIENTS AND THERMODYNAMIC EQUILIBRIUM CONSTANTS FOR CrO_4^{2-}-NO_3^- EXCHANGE ON ZIRCONIUM TRIETHYLAMINE

$X_{CrO_4^{2-}}$	$\bar{X}_{CrO_4^{2-}}$	K_c	K_a
	(a) CrO_4^{2-}-NO_4^- at 30 ± 1°C		
0.0000	0.2364	34.45	
0.0498	0.3745	17.39	
0.1124	0.4516	10.53	
0.1512	0.5344	11.75	
0.2152	0.6180	12.12	
0.2704	0.6888	14.01	26.31
0.3200	0.7446	16.50	
0.3550	0.8459	41.82	
0.4106	0.8772	49.14	
0.5054	0.8874	23.98	

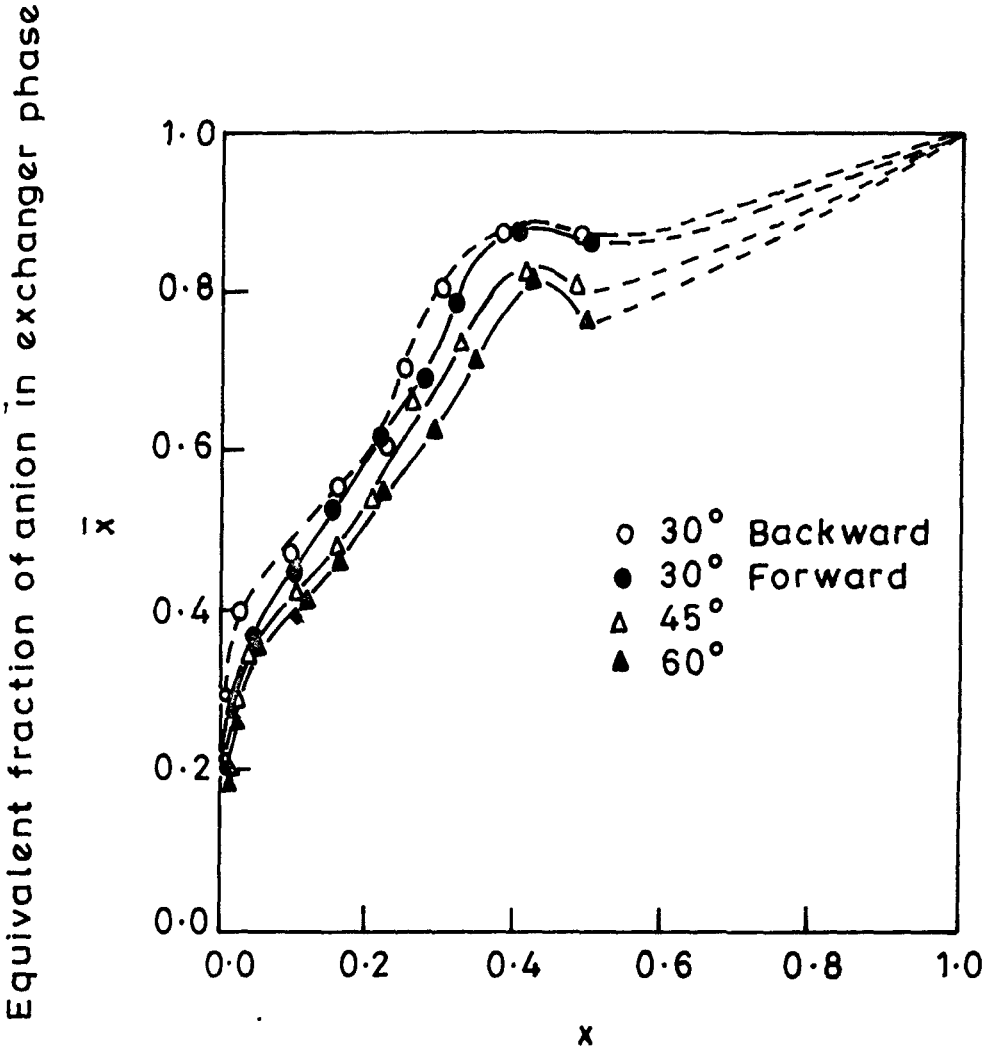

FIG. II ION EXCHANGE ISOTHERM OF CHROMATE IONS ON ZIRCONIUM TRIETHYLAMINE

(Table XIII continued)

$X_{CrO_4^{2-}}$	$\bar{X}_{CrO_4^{2-}}$	K_c	K_a
	(b) CrO_4^{2-}-NO_3^- at 45 ± 1°C		
0.0082	0.2146	33.70	
0.0665	0.3694	13.36	
0.1246	0.4605	9.14	
0.1773	0.4262	9.78	
0.2352	0.6067	10.85	
0.2848	0.6755	11.44	21.04
0.3362	0.7368	14.70	
0.3741	0.8350	32.23	
0.4369	0.8684	35.80	
0.5162	0.8740	18.97	
	(c) CrO_4^{2-}-NO_3^- at 60 ± 1°C		
0.0149	0.2652	32.82	
0.0772	0.3655	10.02	
0.1338	0.4545	8.57	
0.1900	0.5247	8.02	
0.2559	0.5919	7.69	
0.3000	0.6666	9.79	17.68
0.3512	0.7220	11.21	
0.3890	0.8110	21.80	
0.4616	0.8522	23.64	
0.5234	0.8355	13.43	

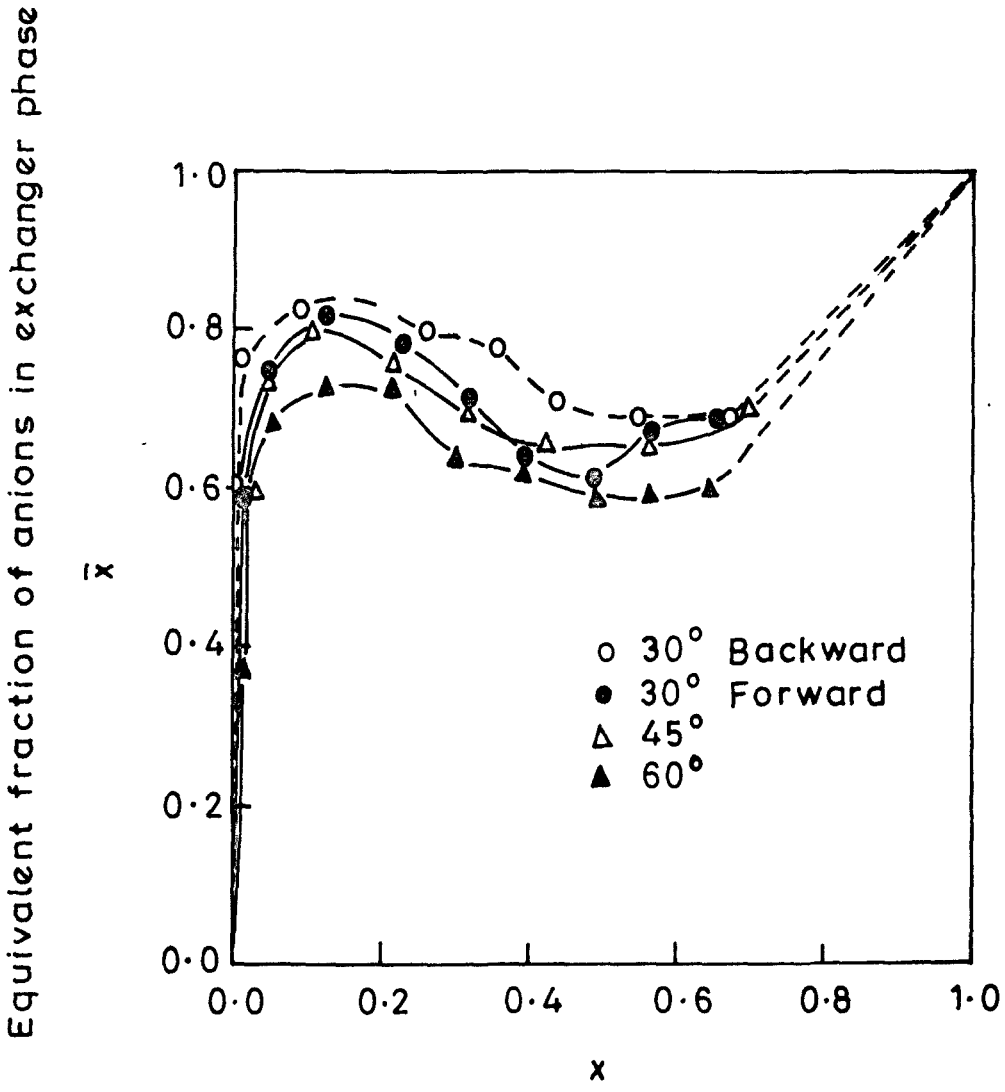

FIG. 12 ION EXCHANGE ISOTHERM OF THIOSULPHATE IONS ON ZIRCONIUM TRIETHYLAMINE

TABLE XIV

EQUIVALENT FRACTIONS OF SO_4^{2-}, SELECTIVITY COEFFICIENTS AND THERMODYNAMIC EQUILIBRIUM CONSTANTS FOR SO_4^{2-}-NO_3^- EXCHANGE ON ZIRCONIUM TRIETHYLAMINE

$X_{SO_4^{2-}}$	$\bar{X}_{SO_4^{2-}}$	K_c	K_a
	(a) SO_4^{2-}-NO_3^- at 30 ± 1°C		
0.0055	0.1526	38.24	
0.0140	0.2576	32.46	
0.0333	0.3488	23.09	
0.0628	0.4777	24.51	
0.1350	0.4890	10.38	
0.2354	0.5173	5.53	5.59
0.3202	0.5555	4.06	
0.4177	0.5990	3.02	
0.4906	0.5722	1.65	
0.6045	0.6150	1.07	
	(b) SO_4^{2-}-NO_3^- at 45 ± 1°C		
0.0068	0.1366	30.76	
0.0250	0.2470	21.05	
0.0446	0.3165	14.86	
0.0825	0.4011	15.07	
0.1466	0.4528	9.13	
0.2429	0.4890	4.39	4.16
0.3260	0.5582	3.15	
0.4204	0.5607	2.38	
0.5050	0.5679	1.42	
0.6173	0.6065	1.04	

(Table XIV continued)

$X_{SO_4^{2-}}$	$\bar{X}_{SO_4^{2-}}$	K_c	K_n
0.0068	0.1245	23.53	
0.0245	0.2288	15.01	
0.0722	0.2686	5.99	
0.1051	0.3455	6.15	
0.1656	0.4227	6.87	
0.2350	0.4555	3.89	2.73
0.3366	0.5600	2.06	
0.4254	0.5350	1.92	
0.5111	0.5624	1.37	
0.6200	0.5892	0.81	

TABLE XV

EQUIVALENT FRACTIONS OF $S_2O_3^{2-}$, SELECTIVITY COEFFICIENTS AND THERMODYNAMIC EQUILIBRIUM CONSTANTS FOR $S_2O_3^{2-}$-NO_3^- EXCHANGE AT ZIRCONIUM TRIETHYLAMINE

$X_{S_2O_3^{2-}}$	$\bar{X}_{S_2O_3^{2-}}$	K_c	K_n
	(a) $S_2O_3^{2-}$-NO_3^- at 30 ± 1°C		
0.0042	0.3745	226.01	
0.0186	0.5924	184.67	
0.0429	0.7494	255.44	
0.1222	0.8228	165.75	
0.2355	0.7812	40.55	
0.3184	0.7156	12.95	19.21
0.4240	0.6490	4.10	
0.4852	0.6004	2.05	
0.5764	0.6550	1.71	
0.6722	0.7000	1.24	

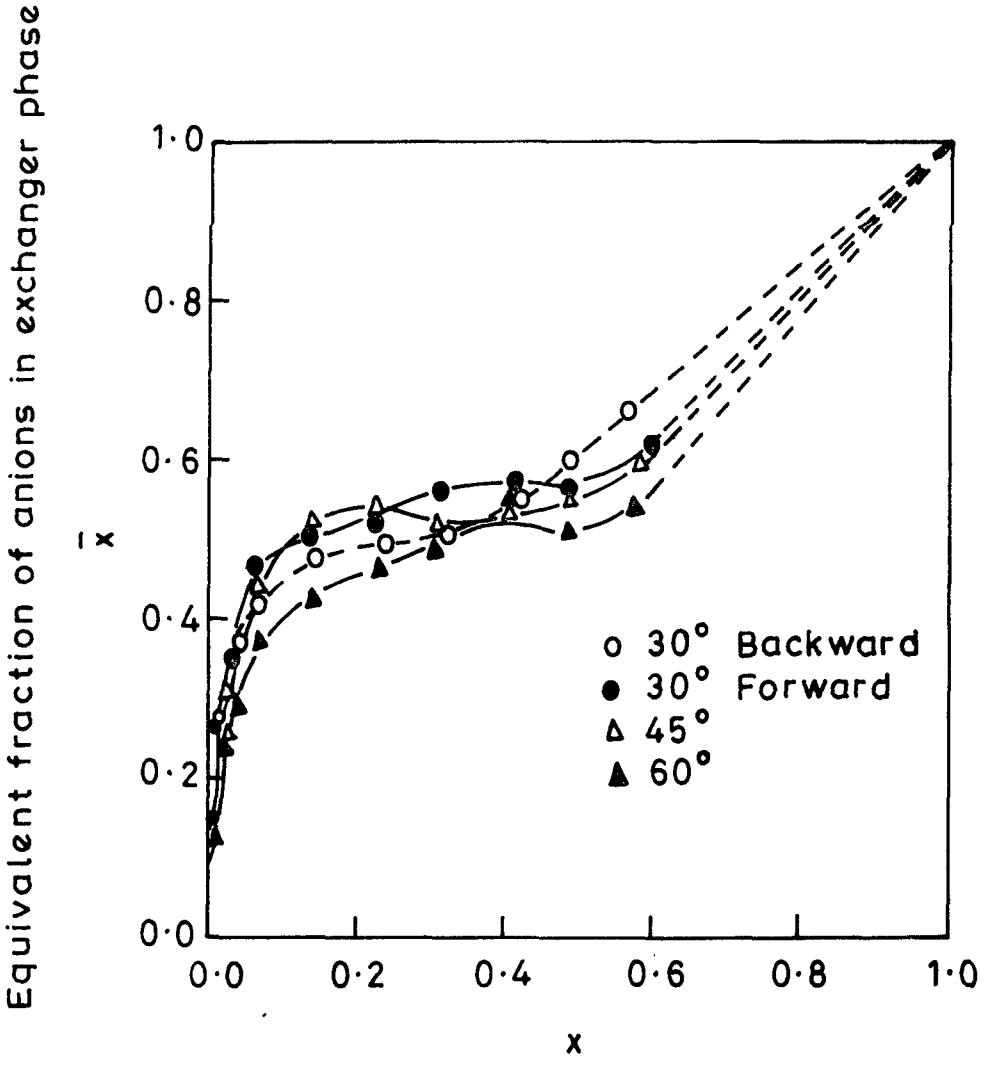

FIG. 13 ION EXCHANGE ISOTHERM OF SULPHATE IONS ON ZIRCONIUM TRIETHYLAMINE

(Table XV continued)

$X_{S_2O_3^{2-}}$	$\bar{X}_{S_2O_3^{2-}}$	K_c	K_a
	(b) $S_2O_3^{2-}$-NO_3^- at 45 ± 1°C		
0.0152	0.3450	211.78	
0.0368	0.5537	154.90	
0.0517	0.7058	198.04	
0.1440	0.7990	153.87	
0.2495	0.7524	36.00	
0.3266	0.6990	11.95	13.88
0.4306	0.6055	4.44	
0.4922	0.5733	1.97	
0.5899	0.6189	1.62	
0.7172	0.7192	1.20	
	(c) $S_2O_3^{2-}$-NO_3^- at 60 ± 1°C		
0.0355	0.3014	194.41	
0.0642	0.5115	127.74	
0.0630	0.6789	151.40	
0.1615	0.7670	145.47	
0.2355	0.7215	34.81	
0.3394	0.6777	11.70	11.19
0.4590	0.5700	4.48	
0.4850	0.5494	1.89	
0.6148	0.5895	1.56	
0.7810	0.7252	1.17	

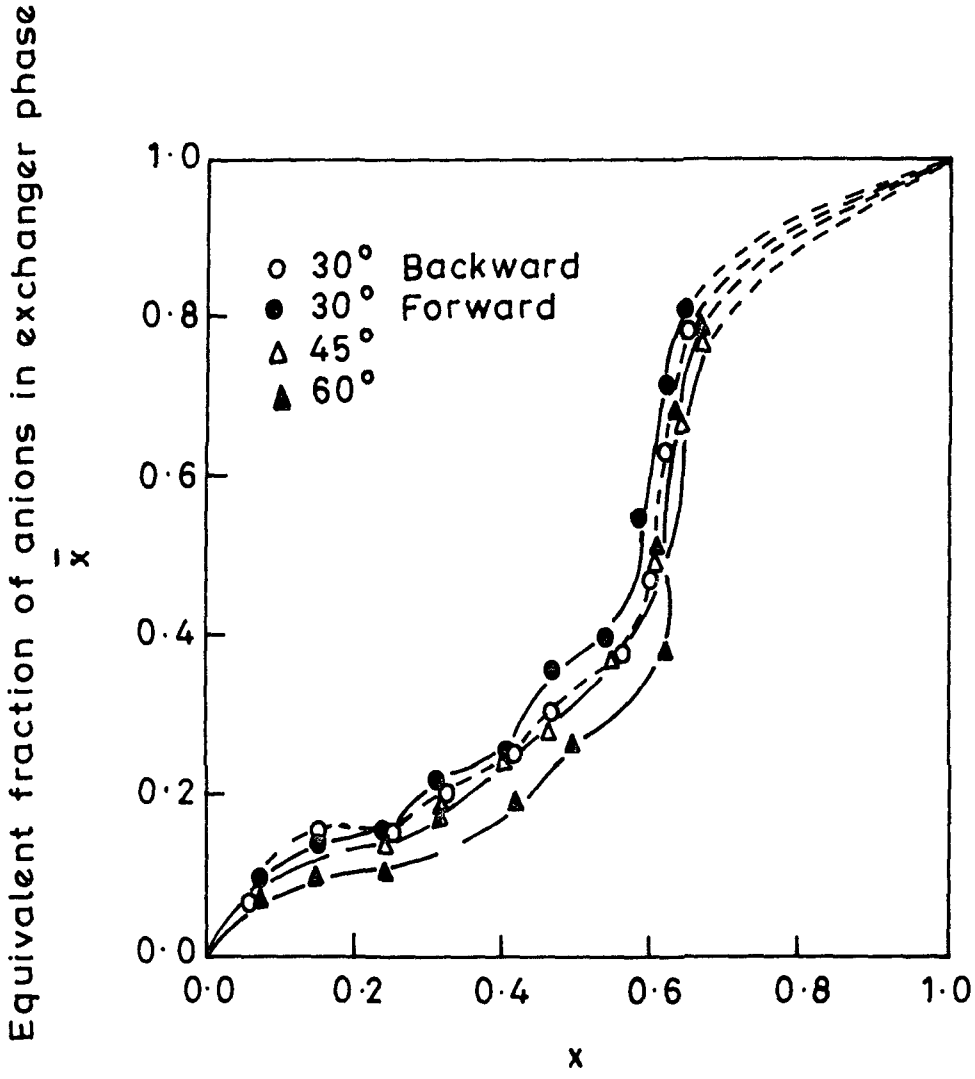

FIG.14 ION EXCHANGE ISOTHERM OF PERMANGANATE IONS ON ZIRCONIUM TRIETHYLAMINE

TABLE XVI

EQUIVALENT FRACTIONS OF MnO_4^-, SELECTIVITY COEFFICIENTS AND THERMODYNAMIC EQUILIBRIUM CONSTANTS FOR $MnO_4^- - NO_3^-$ EXCHANGE ON ZIRCONIUM TRIETHYLAMINE

X_{MnO_4}	$\bar{X}_{MnO_4}$	K_c	K_a
	(a) $MnO_4^- - NO_3^-$ at 30 ± 1°C		
0.0700	0.0800	1.15	
0.1500	0.1300	0.9467	
0.2450	0.1566	0.5718	
0.3200	0.2133	0.5761	
0.4100	0.2600	0.5056	
0.4650	0.3600	0.6471	1.18
0.5550	0.3866	0.5053	
0.5950	0.5466	0.9205	
0.6300	0.7066	1.4144	
0.6800	0.9600	2.8907	
	(b) $MnO_4^- - NO_3^-$ at 45 ± 1°C		
0.0700	0.0800	1.05	
0.1586	0.1105	0.64	
0.2495	0.1470	0.44	
0.3248	0.1722	0.41	
0.4190	0.2177	0.39	
0.4813	0.3212	0.46	0.99
0.5684	0.3568	0.43	
0.6100	0.4375	0.62	
0.6487	0.5290	0.88	
0.6950	0.8282	2.20	

(Table XVI continued)

$X_{MnO_4^-}$	$\bar{X}_{MnO_4^-}$	K_e	K_a
	(e) $MnO_4^- - NO_3^-$ at 60 ± 1 °C		
0.0750	0.0666	0.8800	
0.1650	0.0933	0.5209	
0.2550	0.1200	0.3983	
0.3300	0.1466	0.3487	
0.4300	0.1866	0.3040	
0.5000	0.2667	0.3635	0.74
0.5750	0.3365	0.3584	
0.6350	0.3600	0.3233	
0.6725	0.5252	0.3837	
0.7000	0.8000	1.7142	

The plots of ln K_e versus equivalent fraction of anion in exchanger phase are presented in Figures 15-19. The thermodynamic equilibrium constants calculated from these plots are given in Tables XVI-XVI.

The results of entropy change ΔH°, free energy change ΔG° and entropy change ΔS° were calculated. The results of these thermodynamic parameters are given in Table XVII.

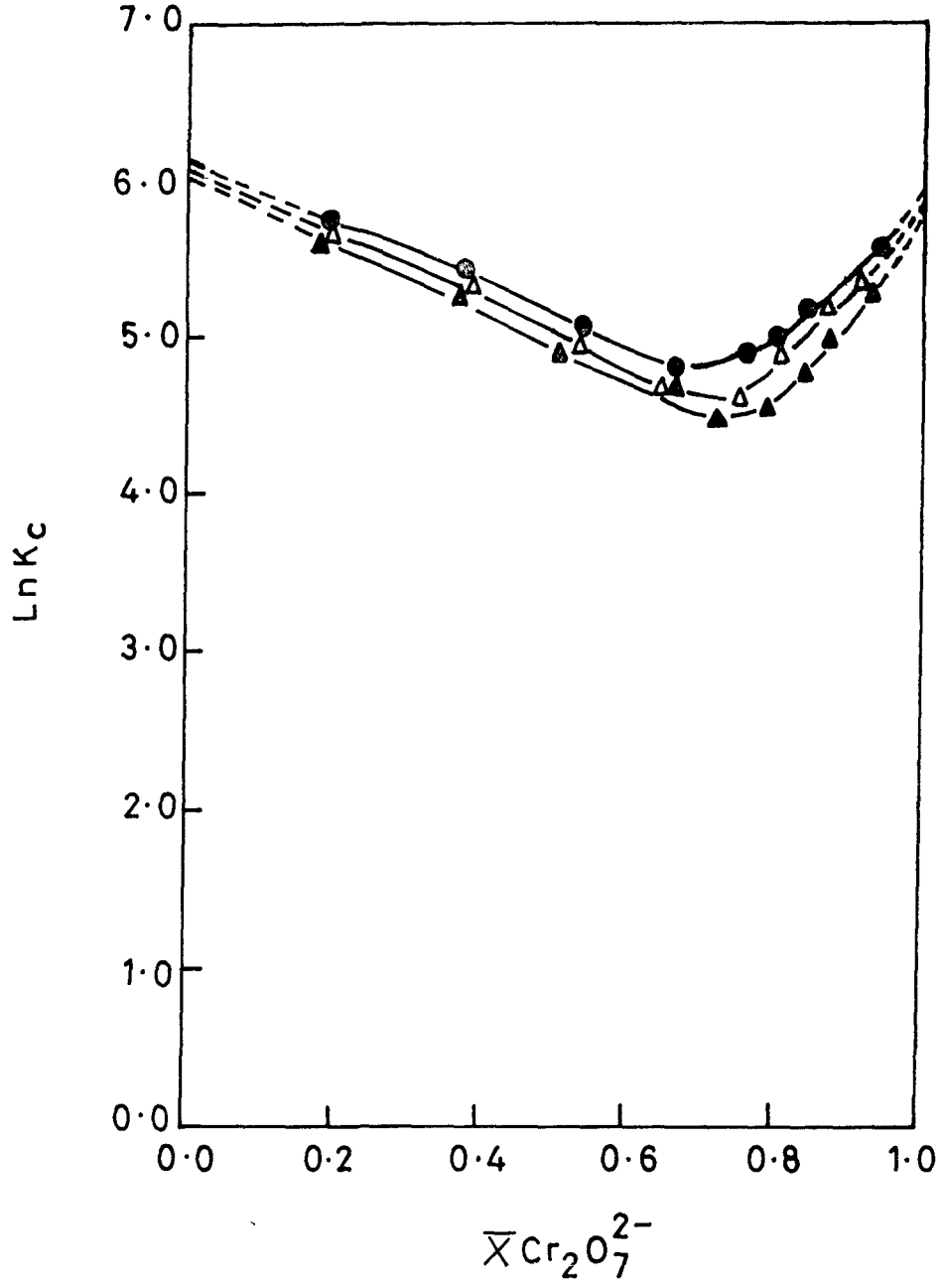

FIG.15 Ln OF SELECTIVITY COEFFICIENTS VS. EQUIVALENT FRACTIONS OF $Cr_2O_7^{2-}$ IN EXCHANGER PHASE

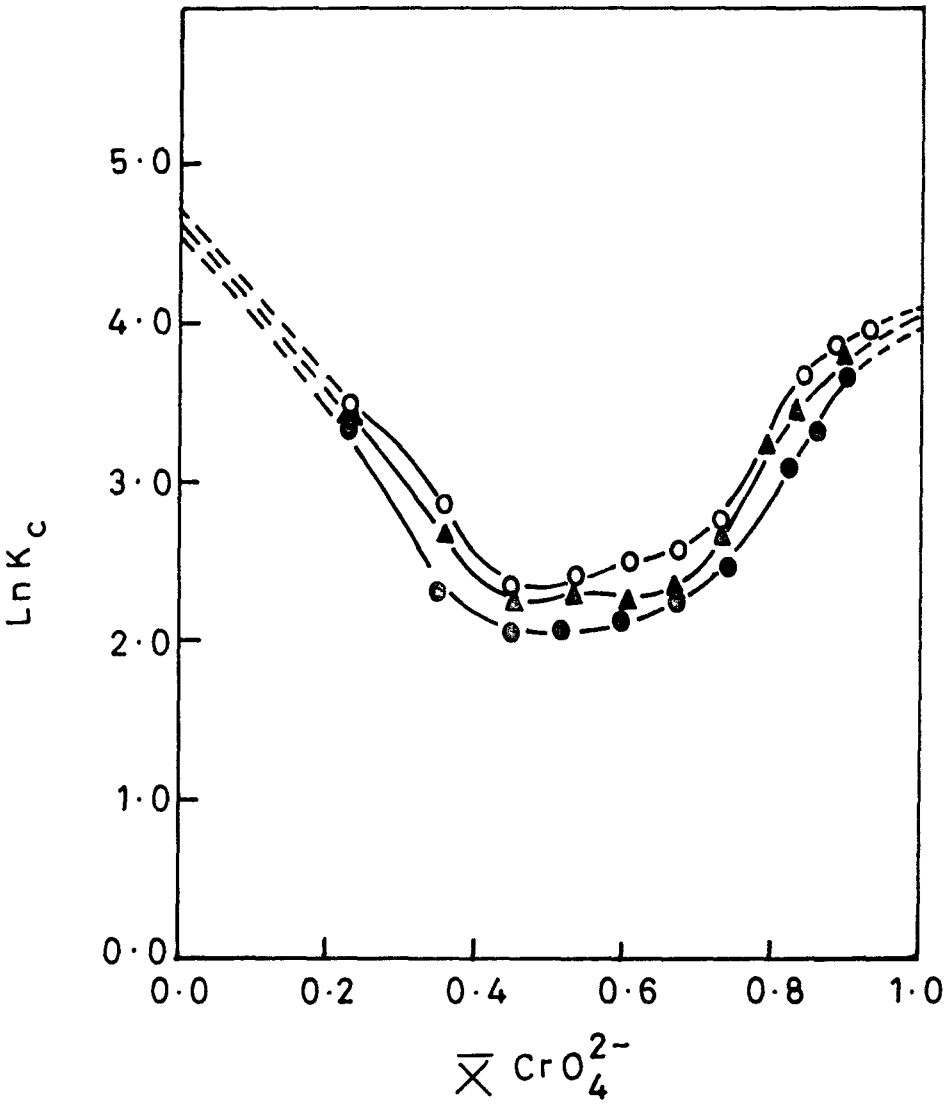

FIG.16 Ln OF SELECTIVITY COEFFICIENTS VS. EQUIVALENT FRACTIONS OF CrO_4^{2-} IN EXCHANGER PHASE

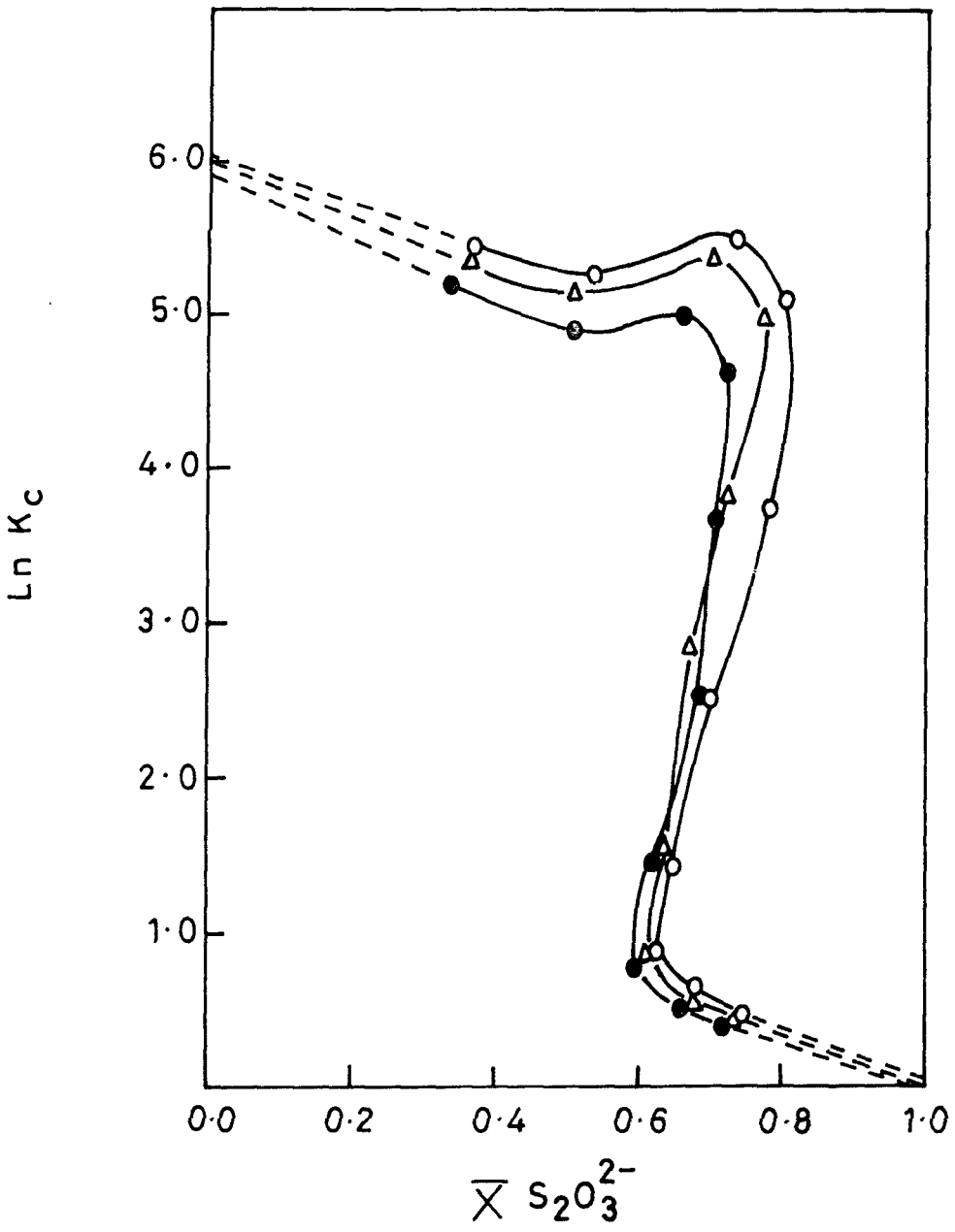

FIG. 17 Ln OF SELECTIVITY COEFFICIENTS VS. EQUIVALENT FRACTIONS OF $S_2O_3^{2-}$ IN EXCHANGER PHASE

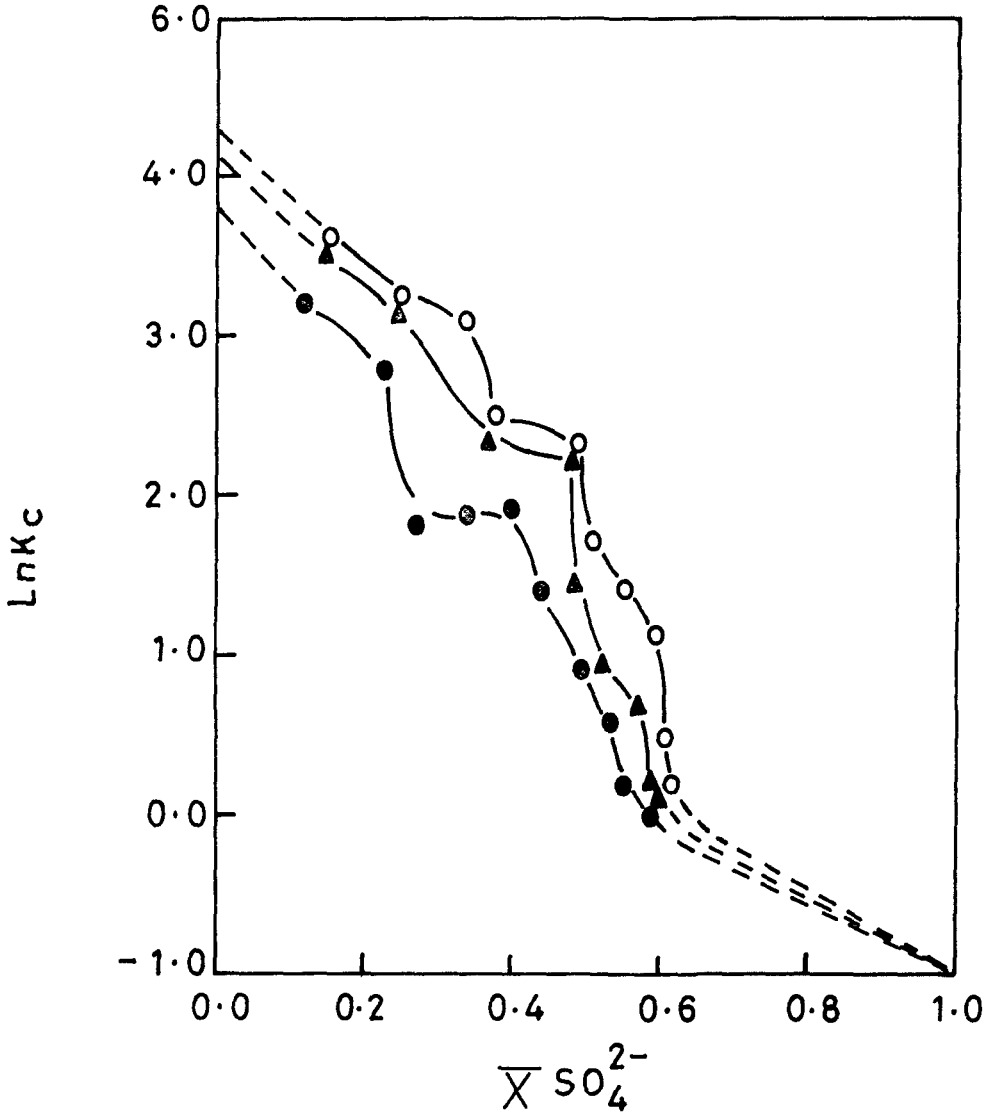

FIG. 18 Ln OF SELECTIVITY COEFFICIENTS VS. EQUIVALENT FRACTIONS OF SO_4^{2-} IN EXCHANGER PHASE

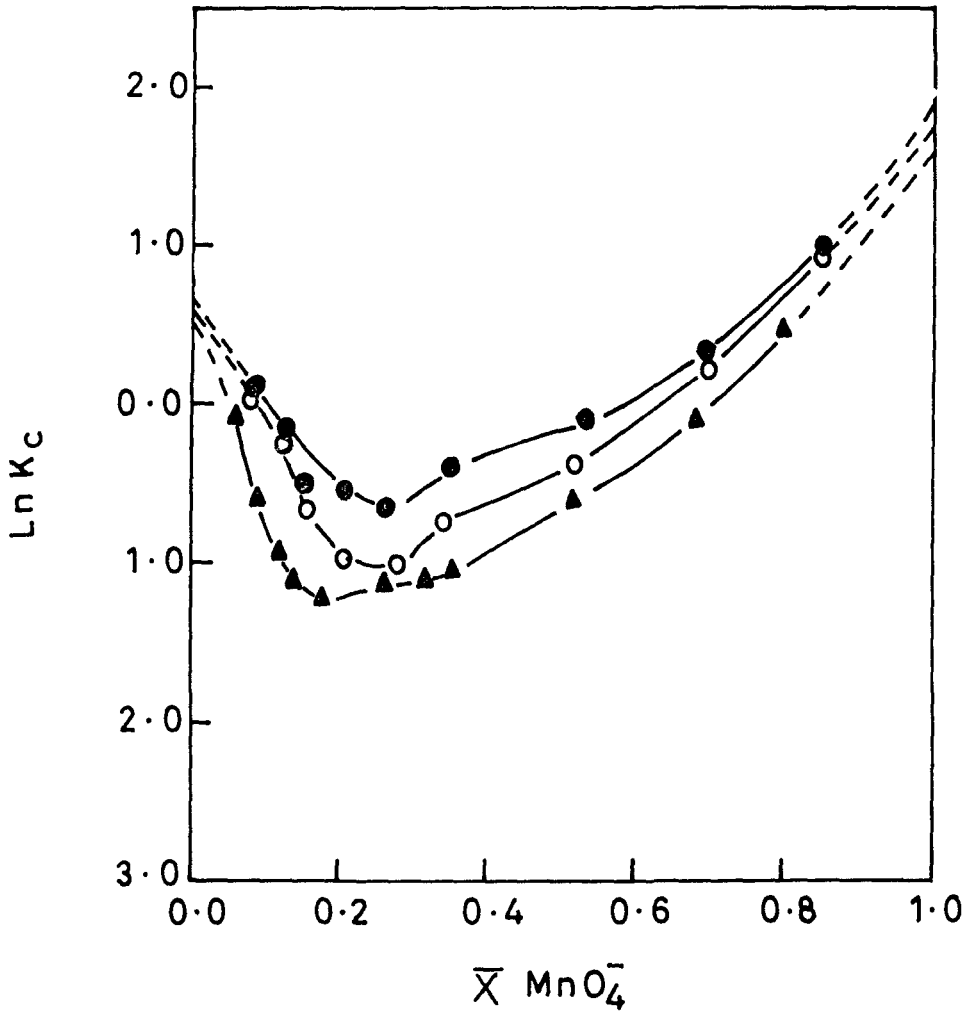

FIG.19 Ln OF SELECTIVITY COEFFICIENTS VS. EQUIVALENT FRACTIONS OF MnO_4^- IN EXCHANGER PHASE

TABLE XVII

THERMODYNAMIC PARAMETERS ON ZIRCONIUM TRIETHYLENE AT AN IONIC STRENGTH OF 0.1 AND VARIOUS TEMPERATURES

Anions	K_a			ΔG°/KJ equiv^{-1}			ΔH°/KJ equiv^{-1} 30-60 °C	ΔS°/J equiv^{-1} deg^{-1}
	30 °C	45 °C	60 °C	30 °C	45 °C	60 °C		
$Cr_2O_7^{2-}$	170.28	64.08	39.25	-12.94	-10.99	-10.16	-4.80	20.80
CrO_4^{2-}	26.31	21.04	17.68	-8.21	-8.06	-7.94	-1.33	21.23
$S_2O_3^{2-}$	19.21	13.98	11.19	-7.43	-6.95	-6.67	-1.50	17.40
SO_4^{2-}	5.59	4.16	2.73	-4.33	-3.75	-2.77	-1.92	5.41
MnO_4^-	1.18	0.89	0.74	-0.40	0.32	0.83	-1.39	-5.09

DISCUSSION

The ion exchange equilibria with certain ion exchangers, especially inorganic ion exchangers can be studied by the application of mass-action law modified in terms of activities. For the exchenger in nitrate form and solution having monovalent counter ion X^- at equilibrium the exchenge may be represented as:

$$\overline{NO_3^-} + X^-_{(aq)} \rightleftharpoons \bar{X}^- + NO_{3(aq)}^- \quad \ldots \quad (1)$$

and for bivalent counter ion

$$2\overline{NO_3^-} + X^{2-}_{(aq)} \rightleftharpoons \bar{X}^{2-} + 2NO_{3(aq)}^- \quad \ldots \quad (2)$$

The thermodynamic equilibrium constant for the above reactions may be written, for uni-univalent exchenge as:

$$K_a = \frac{\bar{a}_{X^-}\ a_{NO_3^-}}{\bar{a}_{NO_3^-}\ a_{X^-}} = \frac{[\bar{X}^-][NO_3^-]}{[\overline{NO_3^-}][X^-]} \cdot \frac{\gamma_{X^-}\ f_{NO_3^-}}{\gamma_{NO_3^-}\ f_{X^-}} \quad \ldots \quad (3)$$

and for uni-bivalent exchenge as:

$$K_a = \frac{(\bar{a}_{X^{2-}})\ (a_{NO_3^-})^2}{(\bar{a}_{NO_3^-})^2\ (a_{X^{2-}})} = \frac{[X^{2-}]\ [NO_3]^2}{[NO_3^-]^2\ [X^{2-}]} \cdot \frac{\gamma_{X^{2-}}\ f_{NO_3^-}^2}{\gamma^2_{NO_3}\ f_{X^{2-}}} \quad \ldots \quad (4)$$

where γ represents activity coefficients in the exchenger phase and f the activity coefficient in the aqueous phase.

An examination of the ion exchange isotherms Figures 10-14 shows that the isotherms are above the diagonal except for MnO_4^- indicating that bivalent anions are strongly preferred in comparison to nitrate by the zirconium triethylamine exchanger. The affinity for the anions decreases as the temperature increases. Figures 10-14 show that all the studied isotherms were reversible whereas the selectivity sequence was

$$Cr_2O_7^{2-} \rangle\ CrO_4^{2-} \rangle\ S_2O_3^{2-} \rangle\ SO_4^{2-} \gg MnO_4^-$$

If K_c is the selectivity coefficient, then for uni-univalent exchange

$$K_c = \frac{\bar{Y}_{X^-}\ X_{NO_3^-}}{\bar{X}_{NO_3^-}\ Y_{X^-}} \cdot \frac{f_{NO_3^-}}{f_{X^-}} \qquad \ldots . \quad (5)$$

and for uni-bivalent exchange

$$K_c = \frac{\bar{Y}_{X^{--}}\ X^2_{NO_3^-}}{\bar{X}^2_{NO_3^-}\ X_{X^{--}}} \cdot \frac{f^2_{NO_3^-}}{f_{X^{--}}} \qquad \ldots . \quad (6)$$

where $\bar{X}_{NO_3^-}$ and $\bar{X}_X$--is the equivalent fraction of competing anions in exchanger phase, $X_{NO_3^-}$ and Y_X--the equivalent fractions of the nitrate and competing anion in solution phase respectively. $f_{NO_3^-}$ and f_{X^-}, the activity coefficients of nitrate and the competing anion respectively in solution. The activity

coefficients of the anions in solution phase were calculated using Debye-Huckel equation

$$\log f_i = \frac{A\, Zi^2 \sqrt{\mu}}{1 + B\, a_i \sqrt{\mu}} \qquad \ldots\ldots \quad (7)$$

where A and B are constants, a_i the ion size parameter, μ the ionic strength and Zi charge of the ion i. The values of A and B at appropriate temperatures are taken from the tables given earlier[8,9].

The results of the selectivity coefficients (Tables XVI-XVI) indicate that as the temperature increases the value of the selectivity coefficient decreases. The results plotted (Figs. 15-19) reveal that the selectivity coefficient K_c does not remain constant at all with the varying concentrations of anions X in solution, and, therefore, K_a should be calculated.

K_a, the thermodynamic equilibrium constant can be obtained according to Gaines and Thomas[10], from the equation:

$$\ln K_a = (Z_{X^-} - Z_{NO_3^-}) + \int_0^1 \ln K_c \, d\bar{X}_X \qquad \ldots\ldots \quad (8)$$

The values of thermodynamic equilibrium constant are calculated by integration under the curves of Figures 15-19 applying equation 8. Variation of ln K_c with loading, $\bar{X}_X$ is given in Figures 15-19. The values of the changes in

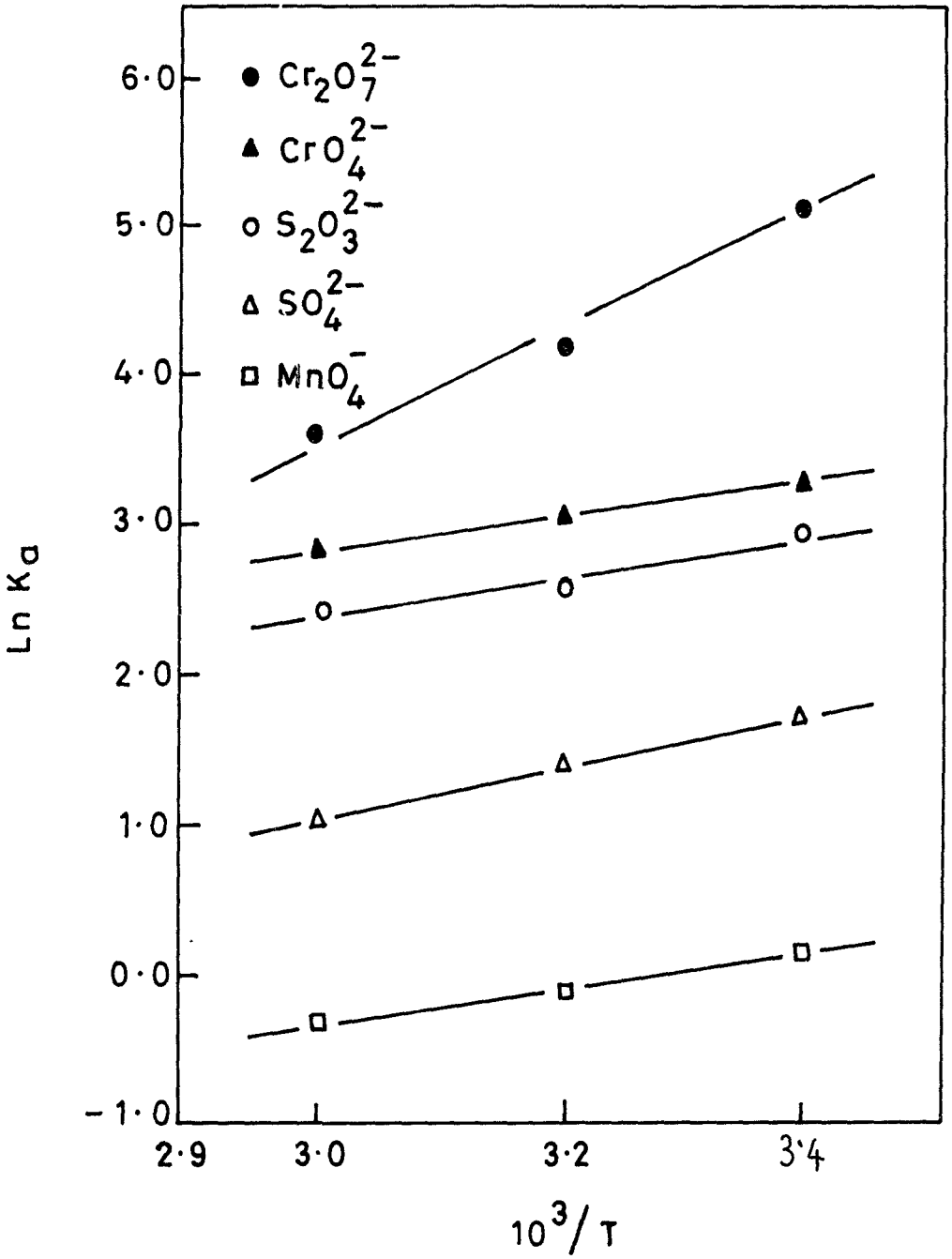

FIG.20 TEMPERATURE DEPENDENCE OF THE THERMODYNAMIC EQUILIBRIUM CONSTANT.

thermodynamic quantities are calculated from the respective thermodynamic equilibrium constants as follows:

$$\Delta G^{\circ} = - RT \ln K_d \quad \ldots\ldots \quad (9)$$

$$\Delta H^{\circ} = - R \frac{d (\ln K_d)}{d (1/T)} \quad \ldots\ldots \quad (10)$$

$$\text{and} \quad \Delta S^{\circ} = (\Delta H^{\circ} - \Delta G^{\circ})/T \quad \ldots\ldots \quad (11)$$

ΔH° is obtained from Figure 20 (expressing the variation of $\ln K_d$ with $1/T$). The results indicate that during the exchange of anions over zirconium triethylamine in nitrate form, the free energy change is negative in all cases except for MnO_4^- at higher temperatures. It reveals that for bivalent anions the exchange process is spontaneous and is in accordance with, mainly, on charge relations. However, for monovalent anion exchange with MnO_4^- the charge being same it may depend on other factors.

The results (Table XVII) giving enthalpy change in all the exchange reactions indicate that process is exothermic i.e. the binding energy of one molecule of competing anion is lower than the two anions of nitrate. Thus the nitrate ion is less tightly bound to the zirconium triethylamine matrix than any of the other anions studied.

The results of entropy changes given in Table XVII indicate that during the forward reaction the competing anionic species are more orderly arranged than that of nitrate form of zirconium triethylamine.

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C H A P T E R - IV

ION EXCHANGE KINETICS OF TRANSITION METAL IONS ON STANNIC OXIDE

Increasing studies on analytical applications of synthetic inorganic ion exchangers show the great importance of these substances. The new materials afford new opportunities in the field of separation science. Besides the development of new materials and their applications interest has also been developed to study the mechanism of ion exchange. Kinetics plays an important role to study the mechanism of ion exchange. Kinetic studies on ion exchange were mainly started by Nachod and Wood[1]. Nancollas and Paterson[2] described the quantitative measurement on hydrous thoria and zirconia. Some studies on kinetics of ion exchange on inorganic ion exchangers have been reported recently[3-9]. To understand the mechanism of ion exchange on granules of stannic oxide, studies are summarized in this chapter. Experimental and theoretical approaches have been used to show the rate of diffusion through the particles. The energy of activation and other parameters are calculated.

EXPERIMENTAL

Reagents

Stannic chloride pentahydrate (Poland) sodium hydroxide (E.Merk) were used. All other reagents were of analaR.

Synthesis of stannic oxide

Stannic oxide was prepared by mixing 0.05M aqueous solution of stannic chloride and sodium hydroxide with constant shaking in the volume ratio 1:2[10]. On standing for 24 hours at room temperature, the white gelatinous precipitate settled down. It was filtered off, washed with demineralized water and dried at 40°C in an oven. The dried product broke down to fine particleswhen immersed in water, washed with water and converted in H^+ form by immersion in 2M nitric acid for 24 hours. It was again washed with demineralized water till free from acid and finally dried at 40°C in an oven.

Kinetic measurements

Rate of exchange were measured by limited bath technique. Stannic oxide was ground well in order to give particles of different mesh size (50-100, 100-150, 150-200 and 200-300). Particles of mesh size (50-100) were used for various studies unless otherwise stated. Solutions of cations were taken in stoppered conical flasks and thermostated at

required temperature. When the required temperature was reached a weighed amount of the exchanger (0.2 g) was added and the flasks were thoroughly shaken. After appropriate intervals the contents of flasks were filtered using Whatman No. 4 filter paper. The ion exchange diffusion studies were conducted at 30°C, 40°C, 50°C and 60°C with ± 1°C variation.

Studied cations Fe^{3+}, Co^{2+}, Mn^{2+} and Zn^{2+} were titrated with EDTA.

RESULTS

The F values as a function of time are calculated and corresponding Bt values are given by Riechenberg[11]. The F and Bt values for Fe^{3+}, Co^{2+}, Mn^{2+} and Zn^{2+} at four different temperatures are given in Tables XVIII-XXI.

TABLE XVIII

F AND Bt VALUES AS A FUNCTION OF TIME FOR DIFFERENT CATIONS ON STANNIC OXIDE AT 30 ± 1°C

t, min	F	Bt	t, min	F	Bt
		Fe^{3+}-H^+ Exchange			
2	0.42	0.20	20	0.93	2.12
5	0.61	0.50	25	0.95	2.54
10	0.77	0.98	30	0.97	3.16
15	0.87	1.54	60	1.00	-
		Mn^{2+}-H^+ Exchange			
2	0.32	0.10	20	0.81	1.15
5	0.46	0.25	25	0.86	1.50
10	0.65	0.60	30	0.89	1.70
15	0.74	0.85	60	0.90	1.80
		Co^{2+}-H^+ Exchange			
2	0.32	0.10	20	0.85	1.40
5	0.50	0.30	25	0.90	1.80
10	0.69	0.70	30	0.93	2.10
15	0.79	1.10	60	-	-
		Zn^{2+}-H^+ Exchange			
2	0.23	0.05	20	0.69	0.70
5	0.38	0.15	25	0.74	0.85
10	0.50	0.30	30	0.76	0.95
15	0.61	0.50	60	-	-

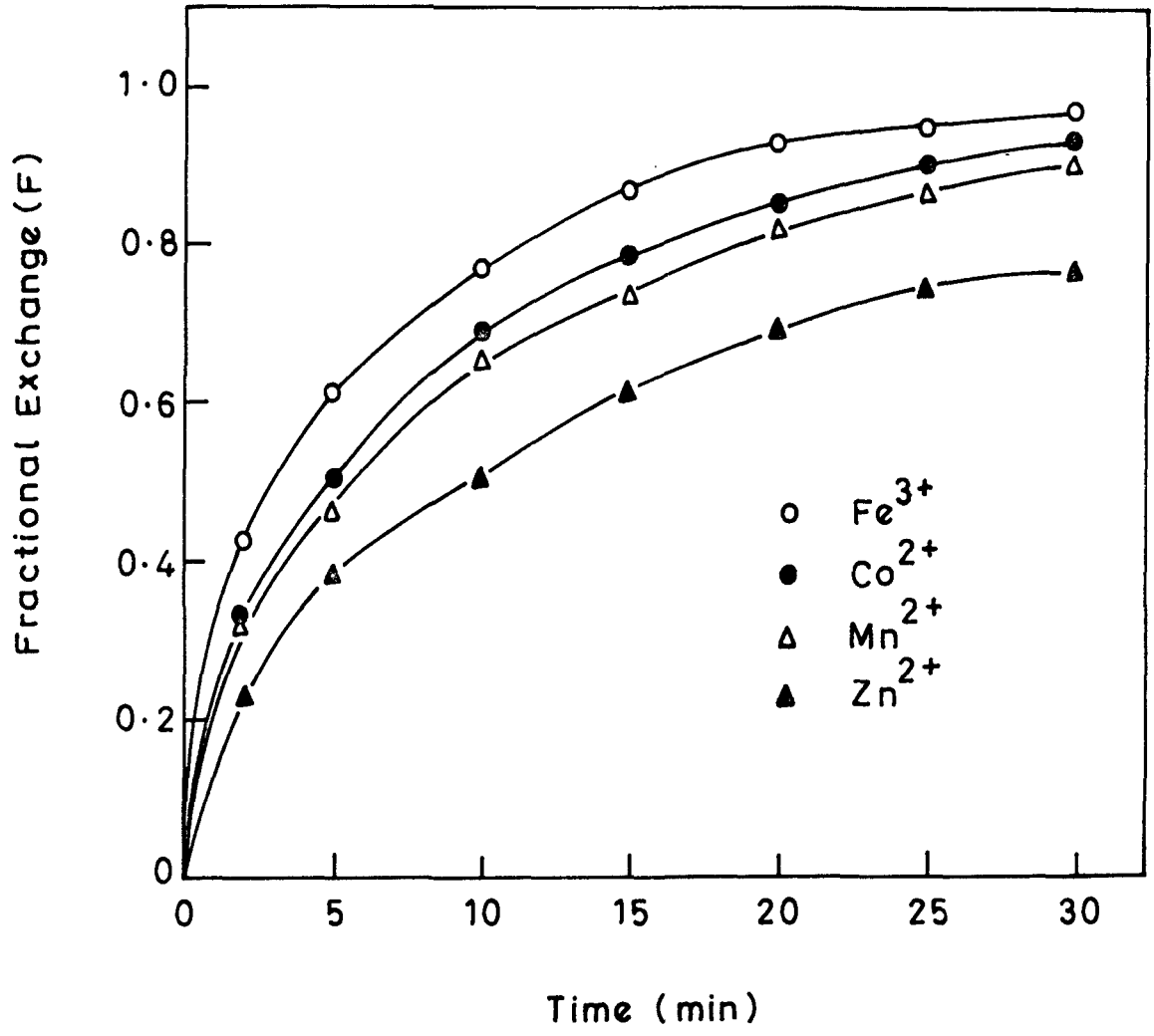

FIG. 21 RATE OF EXCHANGE OF DIFFERENT CATIONS AT 30°C ON STANNIC OXIDE

TABLE XIX

F AND Bt VALUES AS A FUNCTION OF TIME FOR DIFFERENT CATIONS ON STANNIC OXIDE AT 40 ± 1 °C

t,min	F	Bt	t,min	F	Bt
		Fe^{3+}-H^+ Exchange			
2	0.46	0.25	20	0.93	2.25
5	0.63	0.55	25	0.97	2.90
10	0.81	1.20	30	0.98	3.45
15	0.89	1.75	60	-	-
		Mn^{2+}-H^+ Exchange			
2	0.38	0.15	20	0.84	1.35
5	0.50	0.30	25	0.89	1.70
10	0.67	0.65	30	0.92	2.00
15	0.79	1.05	60	-	-
		Co^{2+}-H^+ Exchange			
2	0.38	0.15	20	0.88	1.65
5	0.56	0.40	25	0.92	2.05
10	0.71	0.75	30	0.94	2.40
15	0.80	1.10	60	-	-
		Zn^{2+}-H^+ Exchange			
2	0.23	0.10	20	0.78	1.00
5	0.46	0.25	25	0.83	1.30
10	0.61	0.50	30	0.87	1.55
15	0.71	0.75	60	-	-

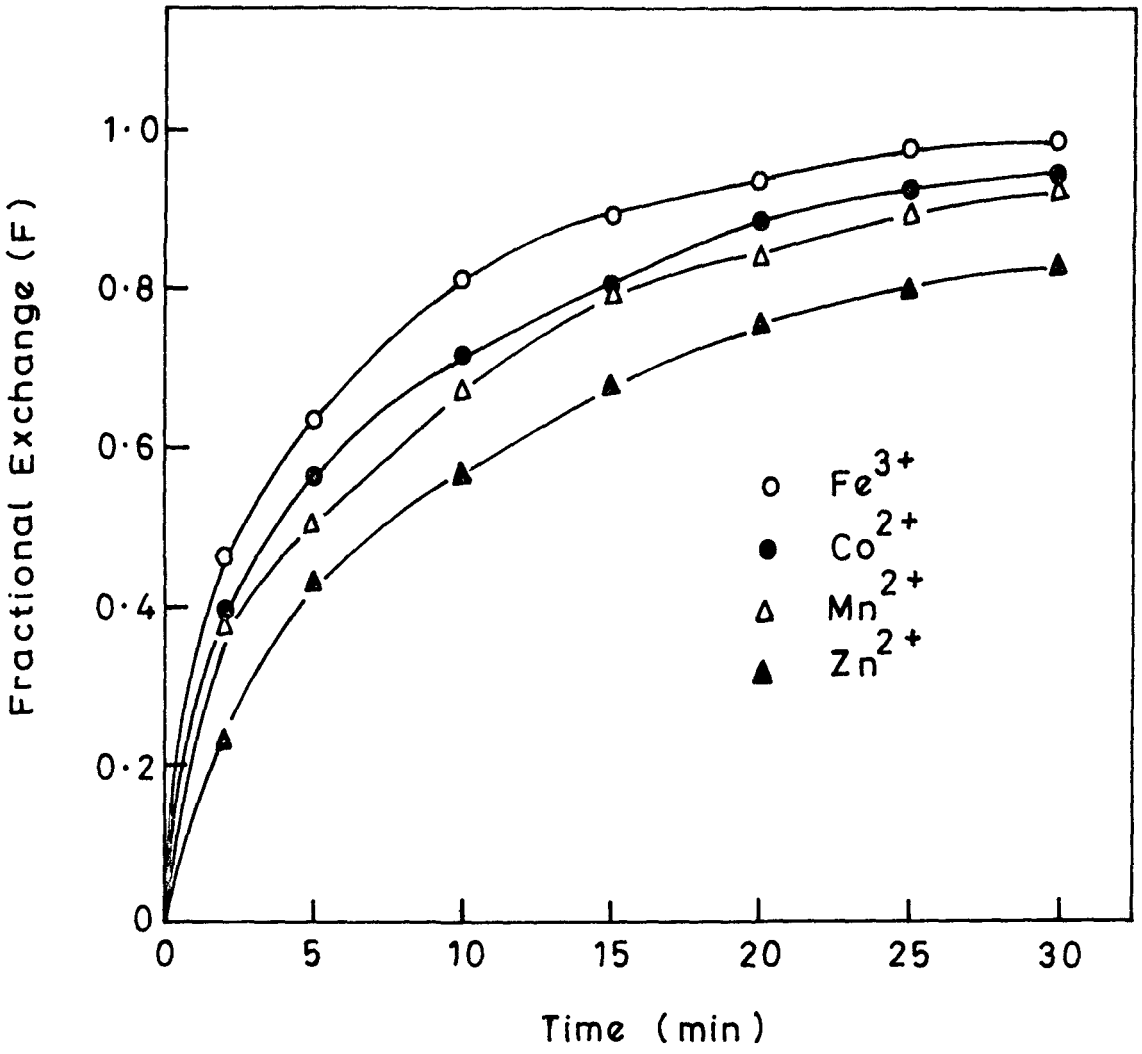

FIG. 22 RATE OF EXCHANGE OF DIFFERENT CATIONS AT 40°C ON STANNIC OXIDE

TABLE XX

F AND Bt VALUES AS A FUNCTION OF TIME FOR DIFFERENT CATIONS ON STANNIC OXIDE AT 50 ± 1 °C

t,min	F	Bt	t,min	F	Bt
		Fe^{3+}-H^+ Exchange			
2	0.50	0.30	20	0.955	2.65
5	0.67	0.65	25	0.975	3.25
10	0.83	1.30	30	0.990	4.11
15	0.91	1.90	60	-	-
		Mn^{2+}-H^+ Exchange			
2	0.42	0.20	20	0.88	1.65
5	0.59	0.45	25	0.92	2.00
10	0.72	0.80	30	0.94	2.40
15	0.83	1.30	60	-	-
		Co^{2+}-H^+ Exchange			
2	0.42	0.20	20	0.90	1.94
5	0.61	0.50	25	0.94	2.36
10	0.78	1.00	30	-	-
15	0.95	1.42	60	-	-
		Zn^{2+}-H^+ Exchange			
2	0.32	0.12	20	0.78	1.03
5	0.46	0.26	25	0.83	1.34
10	0.61	0.53	30	0.87	1.55
15	0.71	0.75	60	-	-

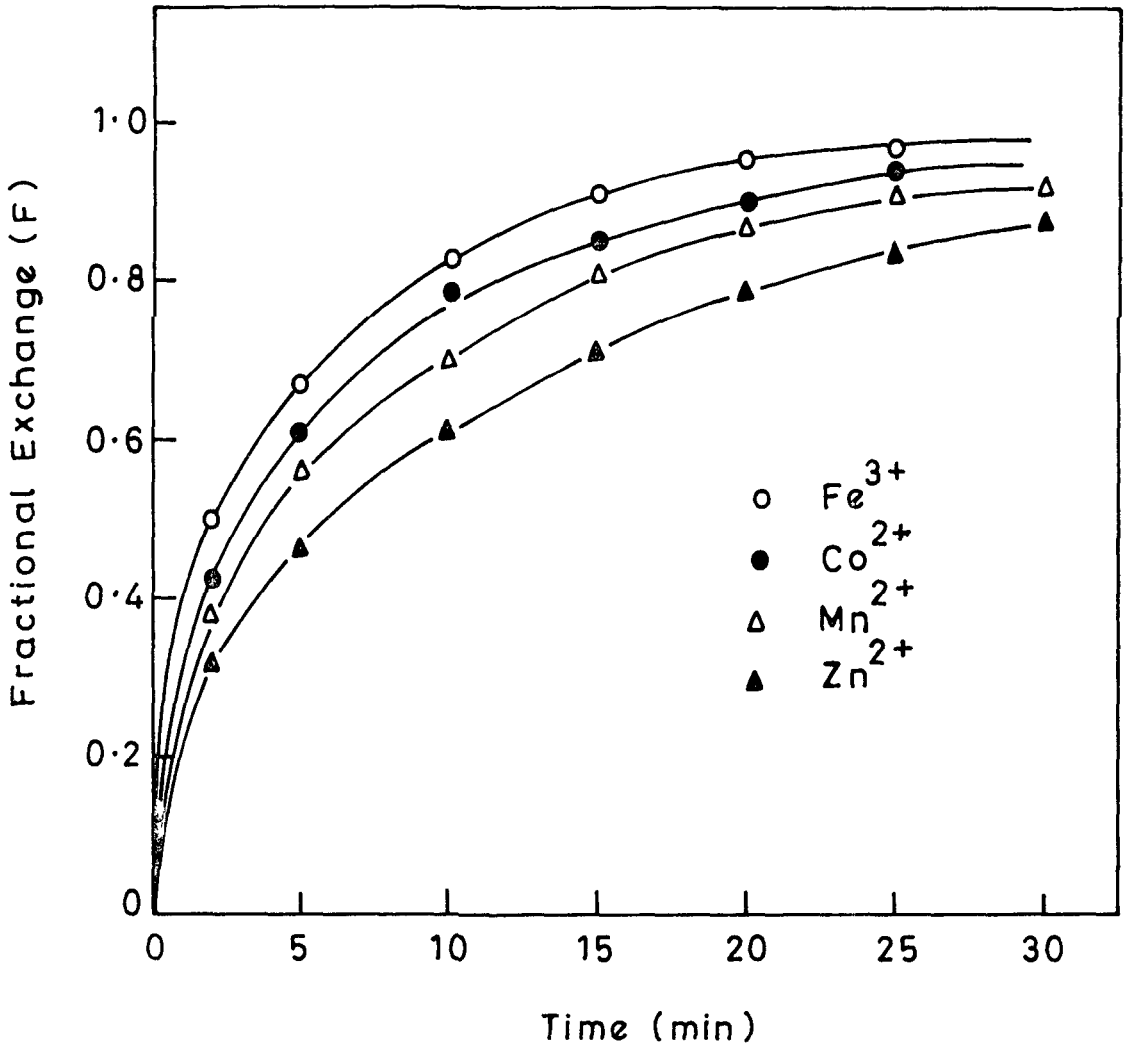

FIG. 23 RATE OF EXCHANGE OF DIFFERENT CATIONS AT 50°C ON STANNIC OXIDE

TABLE XXI

F AND Bt VALUES AS A FUNCTION OF TIME FOR DIFFERENT CATIONS ON STANNIC OXIDE AT 60 ± 1 °C

t,min	F	Bt	t,min	F	Bt
		Fe^{3+}-H^+ Exchange			
2	0.53	0.35	20	0.97	3.00
5	0.72	0.80	25	0.98	3.75
10	0.86	1.50	30	1.00	-
15	0.94	2.30	60	-	-
		Mn^{2+}-H^+ Exchange			
2	0.42	0.22	20	0.88	1.65
5	0.59	0.45	25	0.92	2.06
10	0.72	0.84	30	0.94	2.44
15	0.83	1.33	60	-	-
		Co^{2+}-H^+ Exchange			
2	0.46	0.25	20	0.92	2.13
5	0.61	0.52	25	0.96	2.72
10	0.78	1.05	30	1.00	-
15	0.87	1.55	60	-	-
		Zn^{2+}-H^+ Exchange			
2	0.32	0.14	20	0.81	1.24
5	0.50	0.32	25	0.86	1.45
10	0.65	0.65	30	0.90	1.80
15	0.76	0.95	60	0.96	2.70

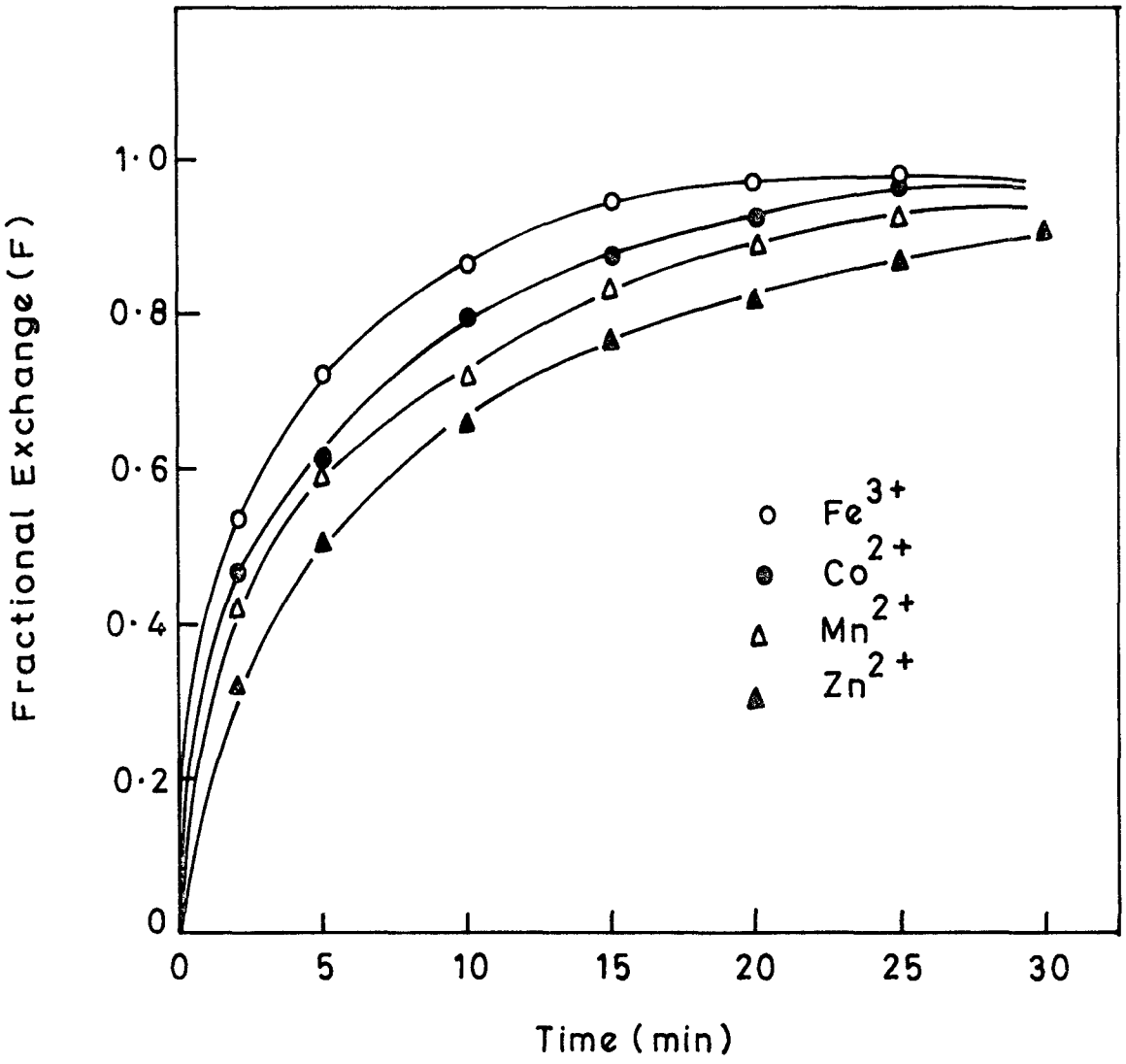

FIG. 24 RATE OF EXCHANGE OF DIFFERENT CATIONS AT 60°C ON STANNIC OXIDE

The values of F at different times and temperatures are presented in Figures 21-24. The Bt values as a function of time for various cations at different temperatures are plotted in Figures 25-28.

The effect of particle size on kinetics of ion exchange for four different particle sizes were performed. The results of F and Bt values as a function of particle size for Fe^{3+}-H^{+} exchange at 30 $\pm$ 1 °C are given in Table XXII. The Bt values as a function of time for Fe^{3+}-H^{+} exchange at 30 $\pm$ 1 °C for four different particle sizes are plotted in Figure 29.

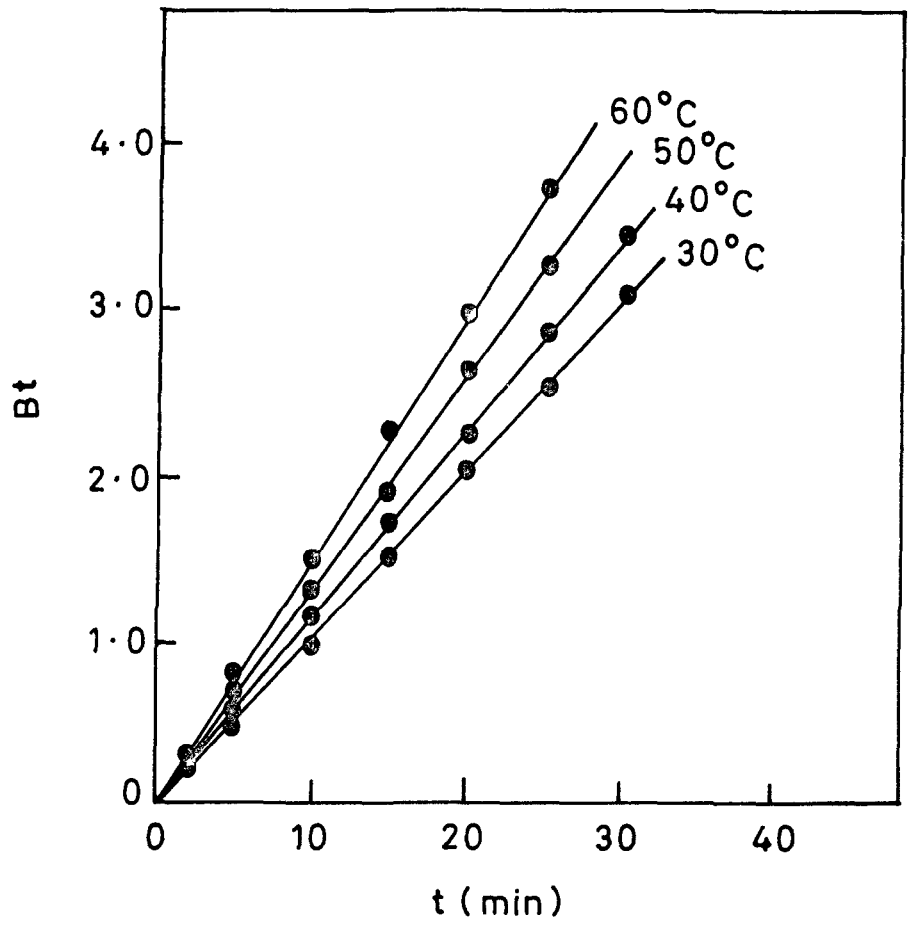

FIG. 25 EFFECT OF TEMPERATURE ON THE RATE OF EXCHANGE FOR Fe^{3+} - H^{+} EXCHANGE ON STANNIC OXIDE

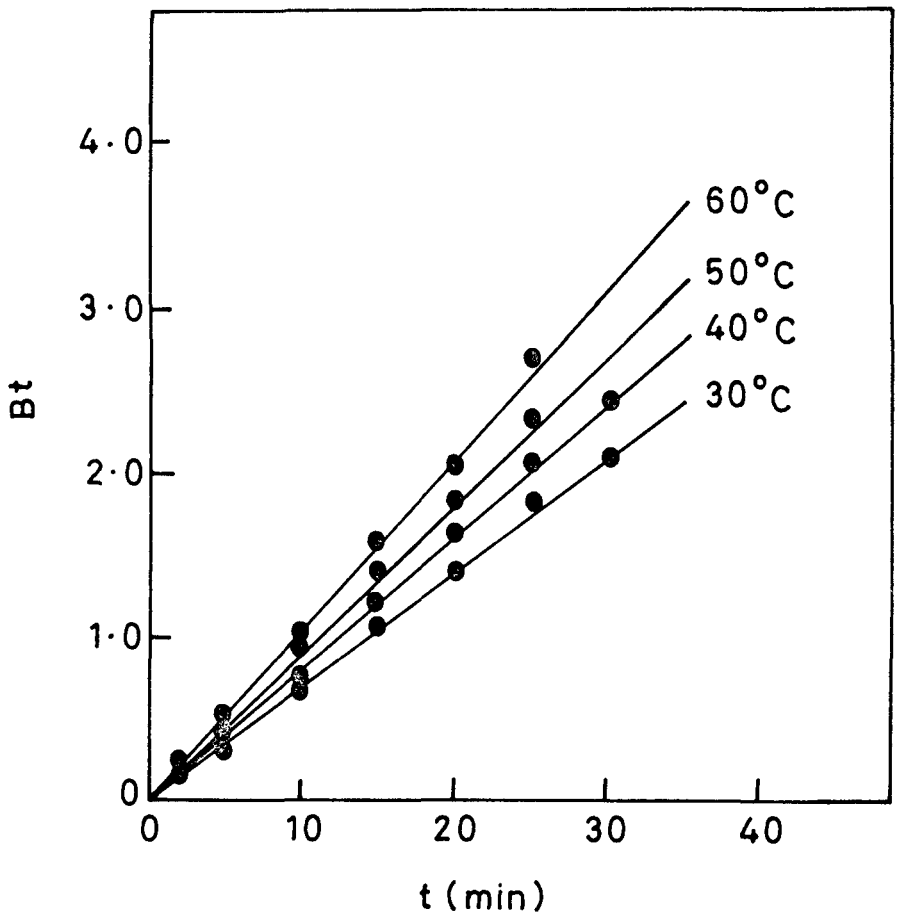

FIG.26 EFFECT OF TEMPERATURE ON THE RATE OF EXCHANGE FOR Co^{2+} - H^{+} EXCHANGE ON STANNIC OXIDE

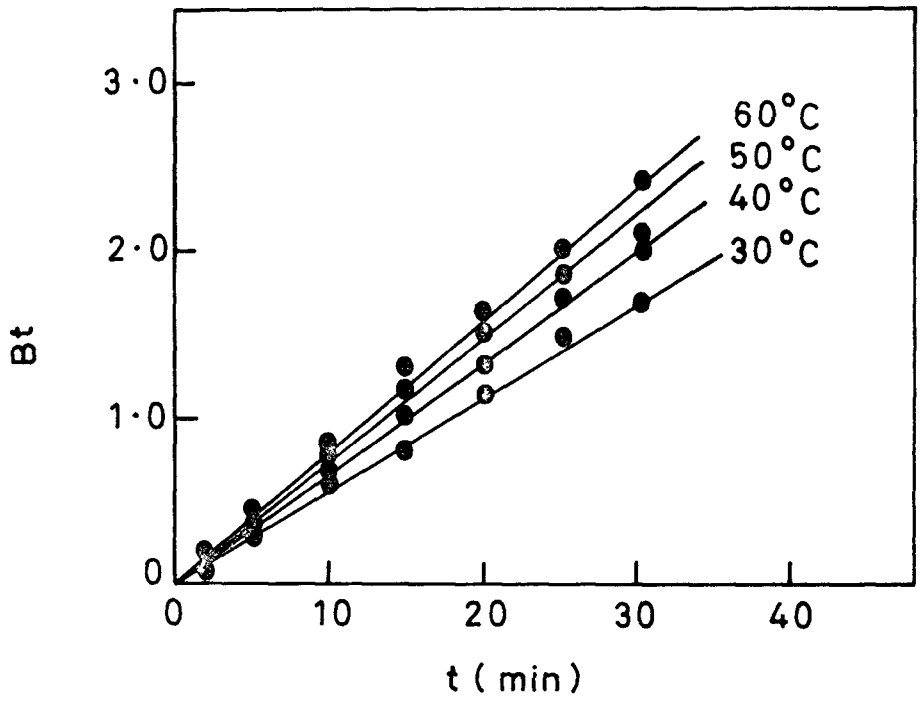

FIG.27 EFFECT OF TEMPERATURE ON THE RATE OF EXCHANGE FOR Mn^{2+}-H^{+} EXCHANGE ON STANNIC OXIDE

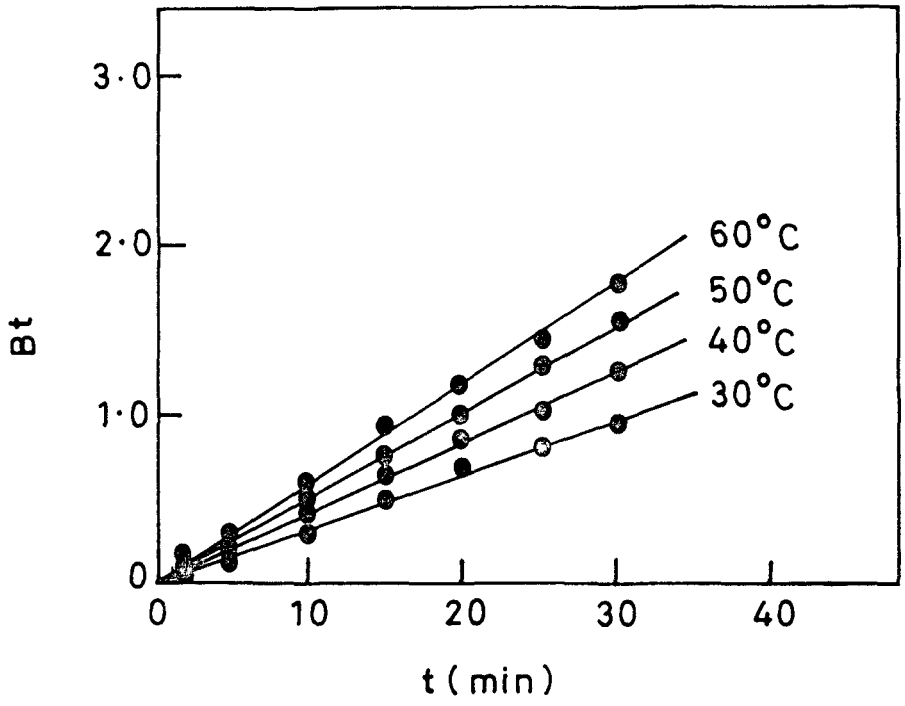

FIG.28 EFFECT OF TEMPERATURE ON THE RATE EXCHANGE OF FOR Zn^{2+}-H^{+} EXCHANGE ON STANNIC OXIDE

TABLE XXII

F AND Bt VALUES AS A FUNCTION OF PARTICLE SIZE FOR Fe^{3+}-H^+ EXCHANGE ON STANNIC OXIDE AT 30 ± 1 °C

t,min	F	Bt	t,min	F	Bt
		For particle size 100 μm			
2	0.46	0.25	20	0.92	2.05
5	0.61	0.50	25	0.955	2.65
10	0.78	1.02	30	0.97	3.16
15	0.88	1.64	-	-	-
		For particle size 60 μm			
2	0.50	0.30	20	0.94	2.35
5	0.65	0.60	25	0.97	3.00
10	0.82	1.20	30	-	-
15	0.89	1.75	-	-	-
		For particle size 42.85 μm			
2	0.53	0.35	20	0.96	2.65
5	0.69	0.70	25	0.98	3.40
10	0.85	1.42	30	-	-
15	0.93	2.14	-	-	-
		For particle size 30 μm			
2	0.56	0.40	15	0.96	2.80
5	0.78	1.04	20	0.98	3.75
10	0.89	1.75	25	-	-

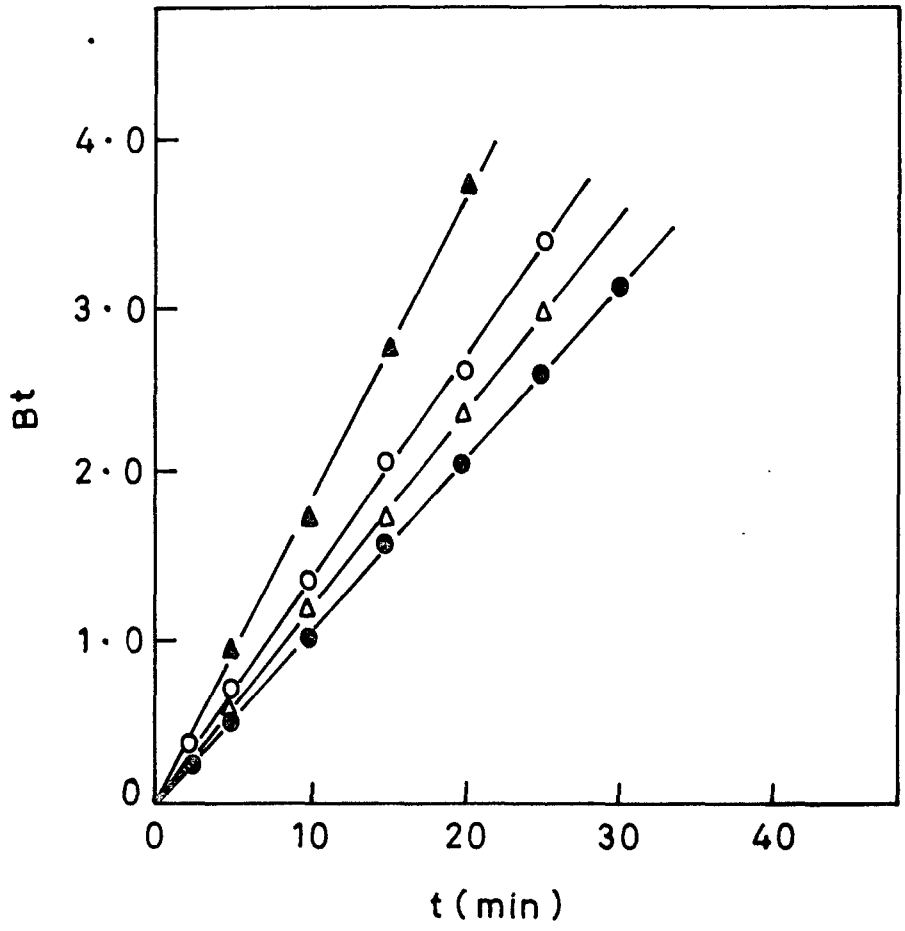

FIG.29 INFLUENCE OF PARTICLE SIZE ON THE RATE OF EXCHANGER FOR Fe^{3+}-H^{+} ON STANNIC OXIDE

● 100 um, Δ 60 um, o 42·85 um, ▲ 30 um

DISCUSSION

To ensure particle diffusion mechanism a study of concentration effect on the rate of exchange for Fe^{3+}-H^+ at 30 ± 1°C was carried out. Since the initial rate of exchange for Fe^{3+}-H^+ is proportional to Fe^{3+} ion concentration at concentrations $< 0.01M$ while at concentrations $> 0.1M$ it is independent of concentration, the studies were made for concentrations greater than 0.1M.

The extent of reaction (F) is defined as:

$$F = \frac{\text{the amount of exchange at time t}}{\text{the amount of exchange at infinite time (equilibrium)}}$$

The values of F at different time intervals and different temperatures were obtained for Fe^{3+}, Mn^{2+}, Co^{2+} and Zn^{2+}-H^+ exchanges and are plotted in Figures 21-24. It is clear from the results that as the temperature increases from 30 to 60°C the rate of ion exchange also increases. This is due to the fact that with increasing temperature mobility of ions increases. These results also indicate that initially the uptake of ions is rapid. The uptake of ion decreases with increase in time. These results are analogous with that of Neither and Markovities[12].

As the rate determining step is exchange through the

ion exchanger particle, the following equation is valid

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{\exp(-n^2 Bt)}{n^2}$$

where

$$B = \pi^2 \, Di/r^2 \qquad \ldots\ldots \qquad (1)$$

r, the radius of the particle, Di is the effective diffusion coefficient of two ions undergoing exchange within exchanger phase[13] and t is the time.

Values of Bt as a function of F may be calculated as tabulated by Reichenberg. The typical Bt versus t plots at different temperatures presented in Tables XVIII-XIX and plotted in Figures 25-28 show that the rate of exchange is directly proportional to the temperature. In all cases the plots Bt versus t are straight lines passing through the origin. This indicates that the rate determining step is diffusion through the exchanger particles at all temperatures studied.

The particle size has a marked effect on the rate of exchange. A plot of Bt versus t at four different particle radii Figure 29 and a plot of B against $1/r^2$ was made in Figure 30 which also comes the straight line indicating that

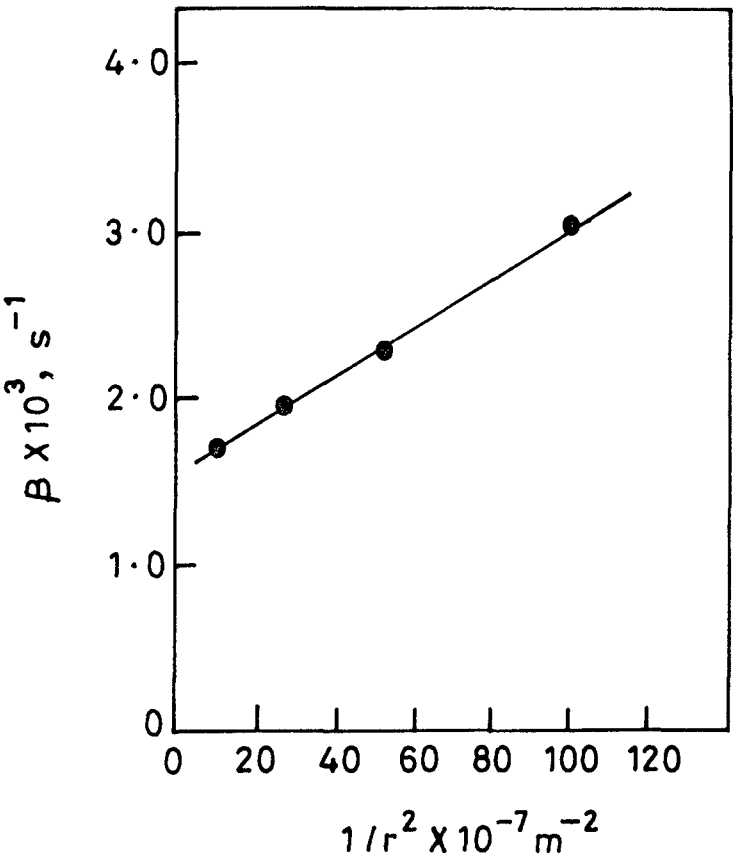

FIG.30 PLOT OF β VS. $1/r^2$ FOR Fe^{3+} AT 30°C

rate of exchange is inversely proportional to the particle radius.

The equation (1) is used for the calculation of the diffusion coefficient (Di). The values are given in Table XXIII. The linear relationship between log Di and 1/T °K (Fig. 31), enables the calculation of the energy of activation (Ea) for the self diffusion of cations to be calculated from Arrhenious equation

$$Di = Do \exp(-Ea/RT) \quad \ldots\ldots \quad (2)$$

TABLE XXIII

VALUE OF Di (cm^2 sec^{-1}) OF VARIOUS IONS AT DIFFERENT TEMPERATURES ON STANNIC OXIDE

Cation	30 °C	40 °C	50 °C	60 °C
Fe^{3+}	1.698×10^{-12}	2.04×10^{-12}	2.29×10^{-12}	2.57×10^{-12}
Co^{2+}	1.20×10^{-12}	1.41×10^{-12}	1.58×10^{-12}	1.69×10^{-12}
Mn^{2+}	9.77×10^{-13}	1.14×10^{-12}	1.31×10^{-12}	1.41×10^{-12}
Zn^{2+}	6.31×10^{-13}	7.58×10^{-13}	8.51×10^{-13}	9.77×10^{-13}

The activation energy of the cation self diffusion process reflects the ease with which cation passes through the

exchanger. The value of activation energy (Ea) for different cations are given in Table XXIV. Calculation of Do and substitution in equation (3) gives entropy of activation ($\triangle S^*$)

$$Do = 2.72\, d^2\, kT/h \exp(\triangle S^*/R) \quad \ldots\ldots \quad (3)$$

where d is the ionic jump distance equal to 5A°, k is the Boltzmann constant equal to 1.38×10^{-23} J $^\circ K^{-1}$ mole^{-1}, h is Planck's constant and T was 273°K. The values of $\triangle G^*$ were obtained from the values of Ea and $\triangle S^*$, which are given in Table XXIV. More negative values of $\triangle S^*$ to divalent ions are analogous to the migration through zeolites[14] and the values of Ea, Do and $\triangle S^*$ give nearly similar pattern to that obtained with other inorganic ion exchangers[7,8,9].

TABLE XXIV

SELF DIFFUSION COEFFICIENTS, ENERGY OF ACTIVATION, ENTROPY OF ACTIVATION AND FREE ENERGY OF ACTIVATION OF METAL IONS ON STANNIC OXIDE (100 µm)

Metal ions	Do $m^2\ s^{-1}$	Ea KJ,mole^{-1}	$\triangle S^*$ J,deg^{-1} mole^{-1}	$\triangle G^*$ KJ,mole^{-1}
Fe^{3+}	1.69×10^{-10}	11.60	-85.42	37.35
Co^{2+}	3.16×10^{-11}	8.05	-202.04	69.25
Mn^{2+}	4.36×10^{-11}	9.41	-94.71	38.10
Zn^{2+}	6.91×10^{-11}	11.70	-90.69	39.23

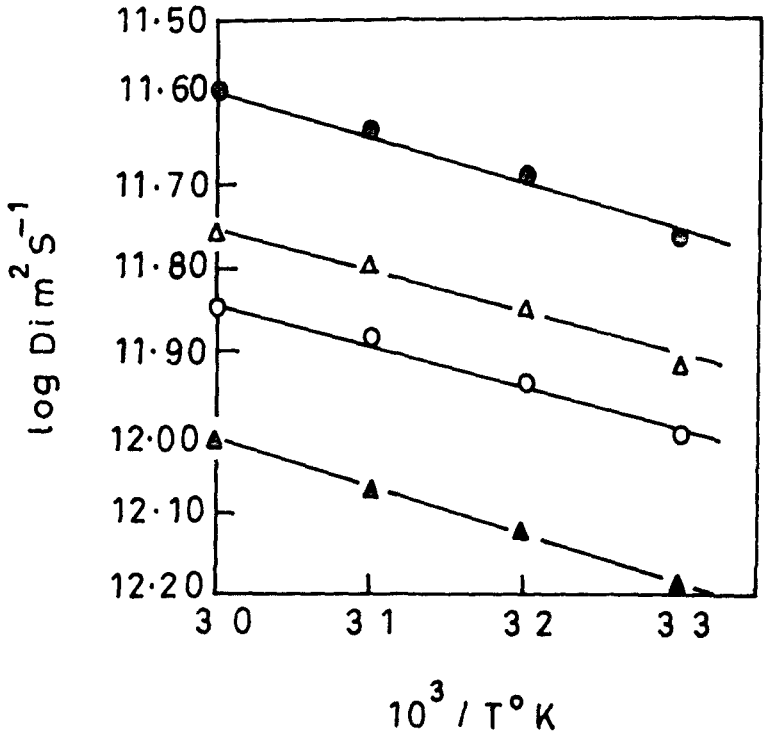

FIG.31 LOG Di VS. 1 / T FOR
● Fe^{3+}, o Mn^{2+}, Δ Co^{2+}, ▲ Zn^{2+}

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C H A P T E R - V

SYNTHESIS, PROPERTIES AND APPLICATIONS OF A NEW INORGANIC ANION EXCHANGER, FERRIC TRIETHYLAMINE

In the continued effort to synthesize a new inorganic anion exchanger based on metal hydroxides with amino group, only a few like amino ethyl phosphate derivative of zirconium[1] has been studied. Some material of this kind have been tried in our laboratories. Aluminium triethanolamine was found to behave as anion exchanger[2]. Thorium triethanolamine as a chelating ion exchanger has also been studied[3]. The studies on thorium-triethylamine and zirconium triethylamine, pave the way to develop some new ion exchanging materials of this type to be utilized for some analytically important separations on the basis of their anion exchange behaviour and for forption of metal ions on the basis of their chelating action. Therefore, the studies are extended to synthesize another material of this kind, ferric triethylamine. The material has been studied for its anion exchange capacity, distribution of different anions to measure selectivity. Composition studies and I.R. studies are made to characterize the exchanger.

EXPERIMENTAL

Apparatus

An electric temperature controlled SICO shaker, Bausch and Lomb spectronic 20 (U.S.A.) and Elico pH meter model LI-10 (India) were used for shaking purpose, spectrophotometric determination and pH measurements respectively.

Reagents

Ferric nitrate (B.D.H.) and triethylamine (E.Merck) were used. The other chemicals were of analytical grade.

Synthesis

Ferric triethylamine was prepared by mixing a 0.1M solution of ferric nitrate and 0.1M triethylamine in the volume ratio of 1:4 (Table XXV). Any alteration in the ratio of the reagents either resulted in the disappearance of the precipitate or the yield was less. Red precipitate thus formed was kept standing at room temperature for 24 hours. The precipitate was filtered and washed with deionized water. It was then dried at 40°C. The dried product was cooled at room temperature for 12 hours. The dried material on immersion in water broke down in small pieces. Again after drying the exchanger was converted in the desired anionic form by treating the exchanger with 1M solution of different anions.

TABLE XXV

CONDITIONS OF PREPARATION AND PROPERTIES OF FERRIC TRIETHYLAMINE EXCHANGER

Samples	Conditions of synthesis		Mixing volume ratio	Properties	
	Molarity of reagents			Nature of precipitate	Anion exchange capacity (meq/gm) for $Cr_2O_7^{--}$
	Ferric nitrate	Triethyl-amine			
S_1	0.1M	0.1M	1:1	No precipitate	-
S_2	0.1M	0.1M	1:2	No precipitate	-
S_3	0.1M	0.1M	2:1	No precipitate	-
S_4	0.1M	0.1M	1:3	Precipitate appears but dissolves	-
S_5	0.1M	0.1M	1:4	A thick precipitate	1.48
S_6	0.1M	0.1M	1:5	Precipitate occurs but disappears on shaking	-
S_7	0.1M	0.1M	2:5	No ppt	-

RESULTS

Anion exchange capacity

The anion exchange capacity of ferric triethylamine exchanger was determined by column method. The anion exchanger weighing one gram was taken in a glass column measuring 20 cm long and 0.6 cm diameter with a glass wool support. The capacity was calculated for different anions namely, chloride, bromide, iodide, dichromate, chromate and sulphate by converting the exchanger in the required form with sodium or potassium salts of required anions. The column was washed with deionized water. The eluent used was 1M sodium nitrate. The elution rate was fixed at 0.5 ml/minute. Table XXVI gives a view of the exchange capacities for different anions.

TABLE XXVI

ION EXCHANGE CAPACITY OF FERRIC TRIETHYLAMINE FOR DIFFERENT ANIONS

Sl. No.	Anions	Salts taken	Capacity (meq/gm)
1.	Chloride	Sodium chloride	0.160
2.	Bromide	Potassium bromide	0.130
3.	Iodide	Potassium iodide	0.105
4.	Dichromate	Potassium dichromate	1.48
5.	Chromate	Potassium chromate	0.74
6.	Sulphate	Sodium sulphate	0.62

Composition

1 gram of ferric triethylamine was dissolved in 50 ml of aquaregia. Heating was avoided for preparing solution. It was then made upto the mark in 100 ml standard flask with deionized water. The amount of iron(III) present in the sample was determined by taking one ml of the solution in the beaker and titrating it against EDTA using PAN indicator. The total amount of iron(III) present in the sample was calculated for 100 ml. Quantitative determination of triethylamine in another portion of the sample was done spectrophotometrically by ninhydrin[4]. Iron and triethylamine were found to be present in the ratio of 1:3 in the exchanger.

Chemical stability

To check the chemical stability of the exchanger ferric triethylamine, 0.5 gm of the exchanger was shaken with different solvents for four hours. The amount of ferric present in the supernatant liquid was determined by titrating a known volume of the solution against EDTA and the amount of triethylamine was determined spectrophotometrically in another sample by ninhydrin. Table XXVII gives the stability of exchanger in different solvent systems.

TABLE XXVII

STABILITY OF FERRIC TRIETHYLAMINE IN DIFFERENT SOLVENTS

Sl. No.	Solvent systems	Solubility (mg/50 ml)	
		Ferric	Triethylamine
1.	Deionized water	00	00
2.	Sodium nitrate (1M)	00	00
3.	Sodium hydroxide (2M)	00	0.01
4.	Ammonium hydroxide (1M)	0.1	0.03
5.	Hydrochloric acid (0.10M)	15.00	31.00
6.	Formic acid (0.10M)	1.50	4.20
7.	Methyl alcohol	00	00
8.	Sulfuric acid	30.00	85.20
9.	Nitric acid (0.10M)	16.00	50.00
10.	Acetic acid (0.10M)	18.20	52.40

Thermal treatment

Different samples of ferric triethylamine were heated in the furnace for 6 hours. The anion exchange capacity for dichromate ions for the exchanger ferric triethylamine at 60°C, 100°C, 150°C, 200°C and 300°C were determined respectively

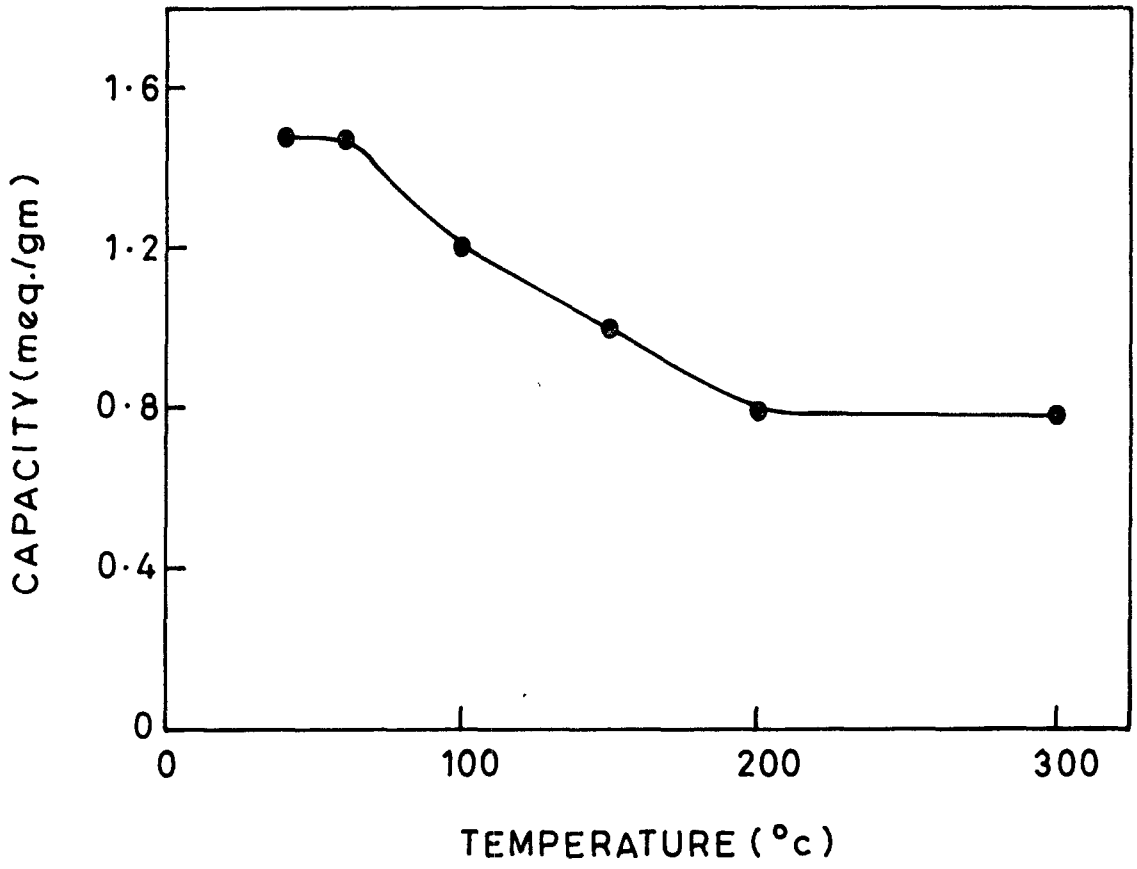

FIG.32 CAPACITY AS A FUNCTION OF TEMPERATURE

(Table XXVIII). In Figure 32 anion exchange capacity (for dichromate ions) were plotted against temperature.

TABLE XXVIII

CAPACITY OF DICHROMATE IONS AT DIFFERENT TEMPERATURES

Sl. No.	Temperature (°C)	Capacity (meq/gm)
1.	40	1.48
2.	60	1.48
3.	100	1.20
4.	150	1.00
5.	200	0.80
6.	300	0.78

Potentiometric studies

pH titrations of the exchanger ferric triethylamine were performed by Topp and Pepper method[5]. 0.5 gm sample of ferric triethylamine was shaken in 250 ml conical flask with 0.01M HCl and 0.01M solution of sodium chloride. The volume of both the solution was kept 50 ml in each case. Each flask was then equilibrated for four hours and then pH of each solution was determined by pH meter. Figure 33 gives the curve for the pH titration.

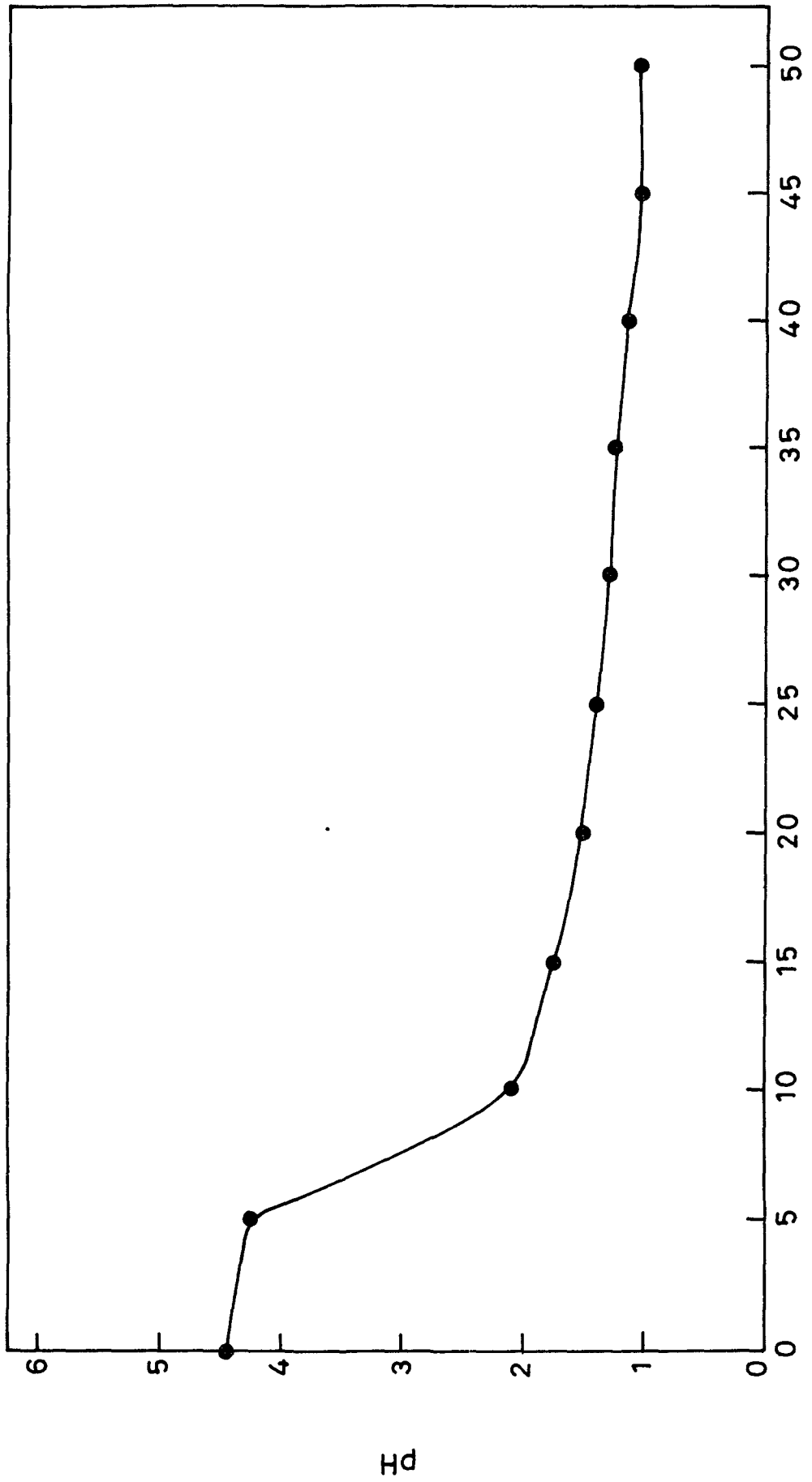

FIG.33 pH TITRATION CURVE FOR IRON TRIETHYLAMINE EXCHANGER

I.R. studies

For characterizing ion exchanger, I.R. studies were made. I.R. spectrum of ferric triethylamine were performed by using KBr disc. Figure 34 shows the spectrum.

Distribution studies

Kd values for anions were determined by bach process. 1 ml of 0.3" anionic solution and 49 ml of the solution in which Kd values of the exchanger were to be checked, were added in a 250 ml erlenmeyer flask. 0.5 gm of the exchanger was then added in the flasks. These flasks were then shaken for 4 hours in a shaker for obtaining complete equilibrium. The anions left in solution were then determined. Total amount of anions were also determined without equilibration. Kd values can be calculated by using the formula

$$Kd = \frac{I-F}{F} \times \frac{\text{Volume of the solution}}{\text{Weight of the exchanger}}$$

where I = Initial volume of titrant before equilibration, and

F = Final volume of titrant after equilibration.

Kd values in deionized water and different molar solutions of sodium hydroxide are reported in Table XXIX.

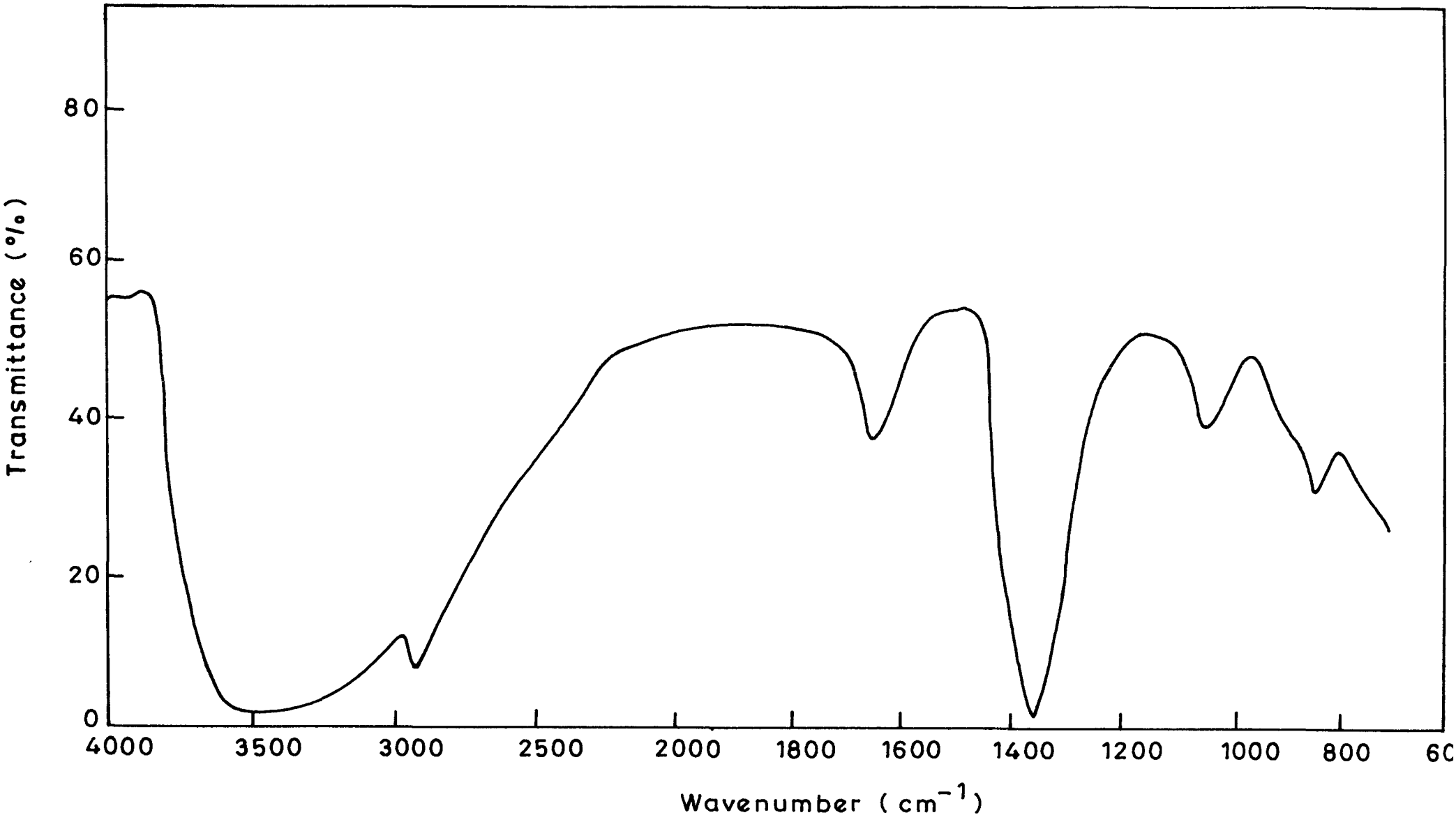

FIG. 34 I.R. SPECTRUM OF IRON TRIETHYLAMINE EXCHANGER.

TABLE XXIX

Kd VALUES FOR DIFFERENT ANIONS IN DIFFERENT SOLVENTS

Sl. No.	Anions	Kd				
		Water	NaOH (10^{-4}M)	NaOH (10^{-3}M)	NaOH (10^{-2}M)	NaOH (10^{-1}M)
1.	Chloride	100	81	41	32	13
2.	Bromide	64	57	23	12	5
3.	Iodide	101	84	47	10	01
4.	Dichromate	T.A.	T.A.	T.A.	8	4
5.	Chromate	T.A.	3666	1800	10	7
6.	Thiocyanate	220	129	52	85	00
7.	Thiosulfate	233	150	91	08	02
8.	Iodate	1440	1440	280	15	10
9.	Bromate	1670	286	86	70	52
10.	Arsenate	3450	3480	1300	536	51
11.	Chlorate	1290	1120	295	280	115
12.	Sulfate	224	205	114	114	42
13.	Sulfate	1200	1250	234	42	12
14.	Persulfate	233	150	67	50	30
15.	Ferrocyanide	553	553	138	27	12
16.	Phosphate	T.A.	1890	54	40	02
17.	Arsenite	T.A.	T.A.	560	420	40

Separations

Owing to the large differences in K_d values for different anions, many analytically important separations of anions were tried and successfully achieved. The columns having a height of 30 cms and diameter 0.60 cm fitted with the glass wool in the bottom were used. 2.0 gm of the exchanger having 150-200 mesh size in nitrate form was added into the column. The mixture of anion solutions was added in the column for separation. The solution was allowed to trickle down slowly through the column. The solution was repeatedly passed through the column to ensure complete adsorption of anions. These anions were adsorbed at the top of the exchanger bed. The anions were then eluted by appropriate eluting reagent. The amount of anions were then determined by standard methods. Separations of CrO_4^{--} from I^-, $Cr_2O_7^{--}$ from Br^-, SO_4^{--} from I^-, $Cr_2O_7^{--}$ from Cl^-, CrO_4^{--} from Br^- were successfully achieved. The elution curves for each set of separation are shown in Figure 35. Table XXX gives a view of quantitative separation of anion on ferric triethylamine columns.

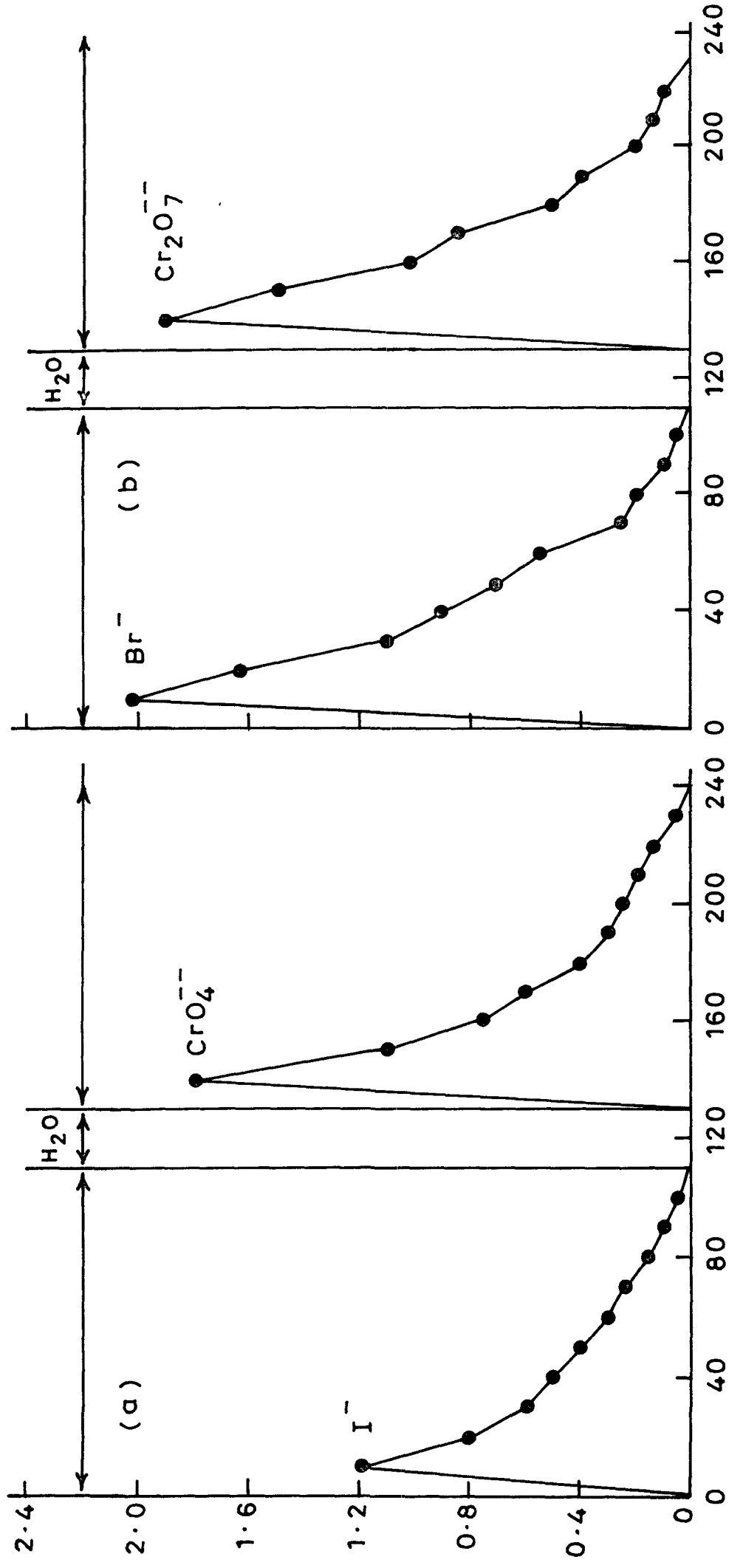

FIG. 35 (a) SEPARATION OF I^- FROM CrO_4^{--}
(b) SEPARATION OF Br FROM $Cr_2O_7^{--}$

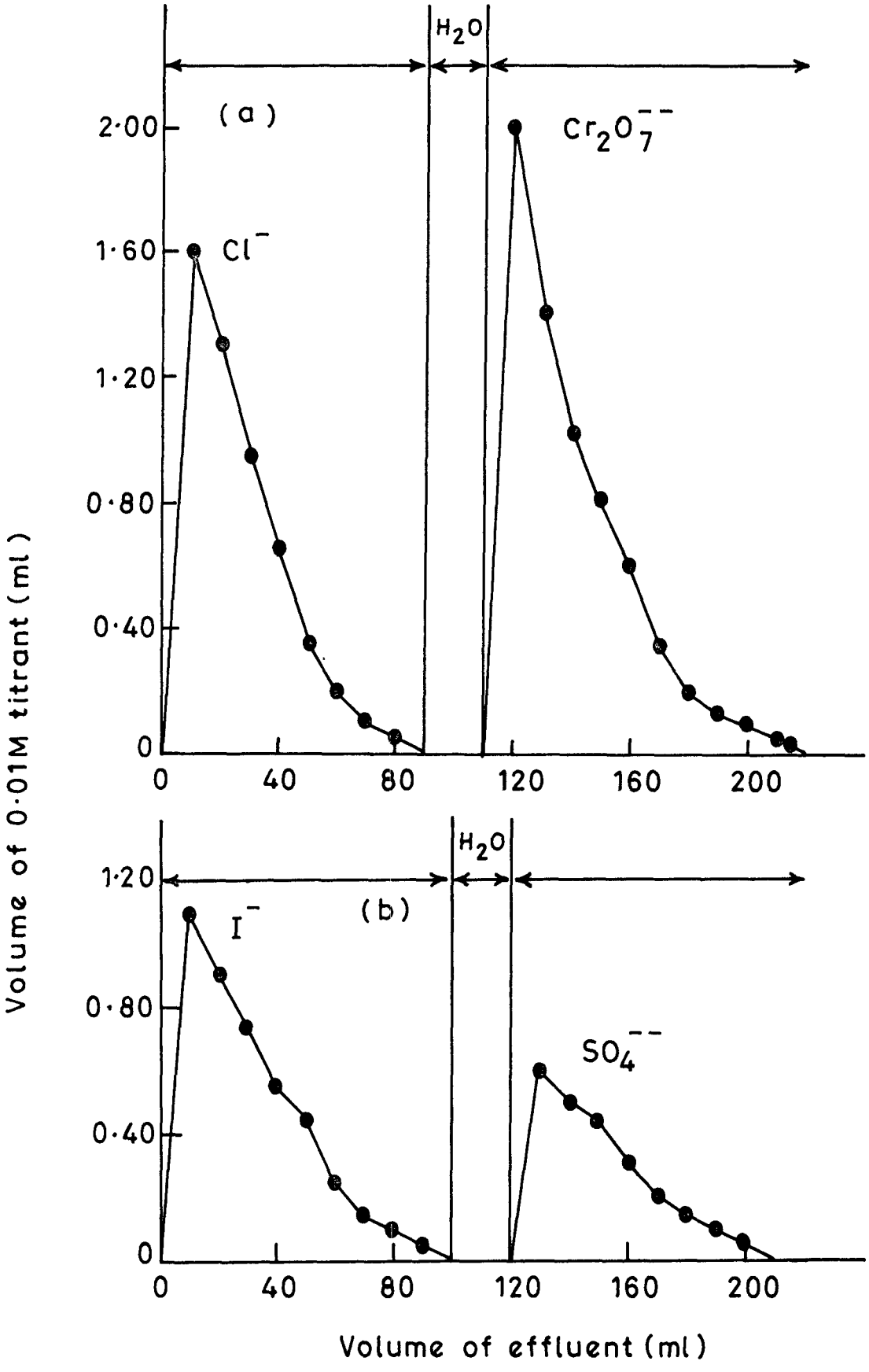

FIG.36(a) SEPARATION OF Cl^- FROM $Cr_2O_7^{--}$

(b) SEPARATION OF I^- FROM SO_4^{--}

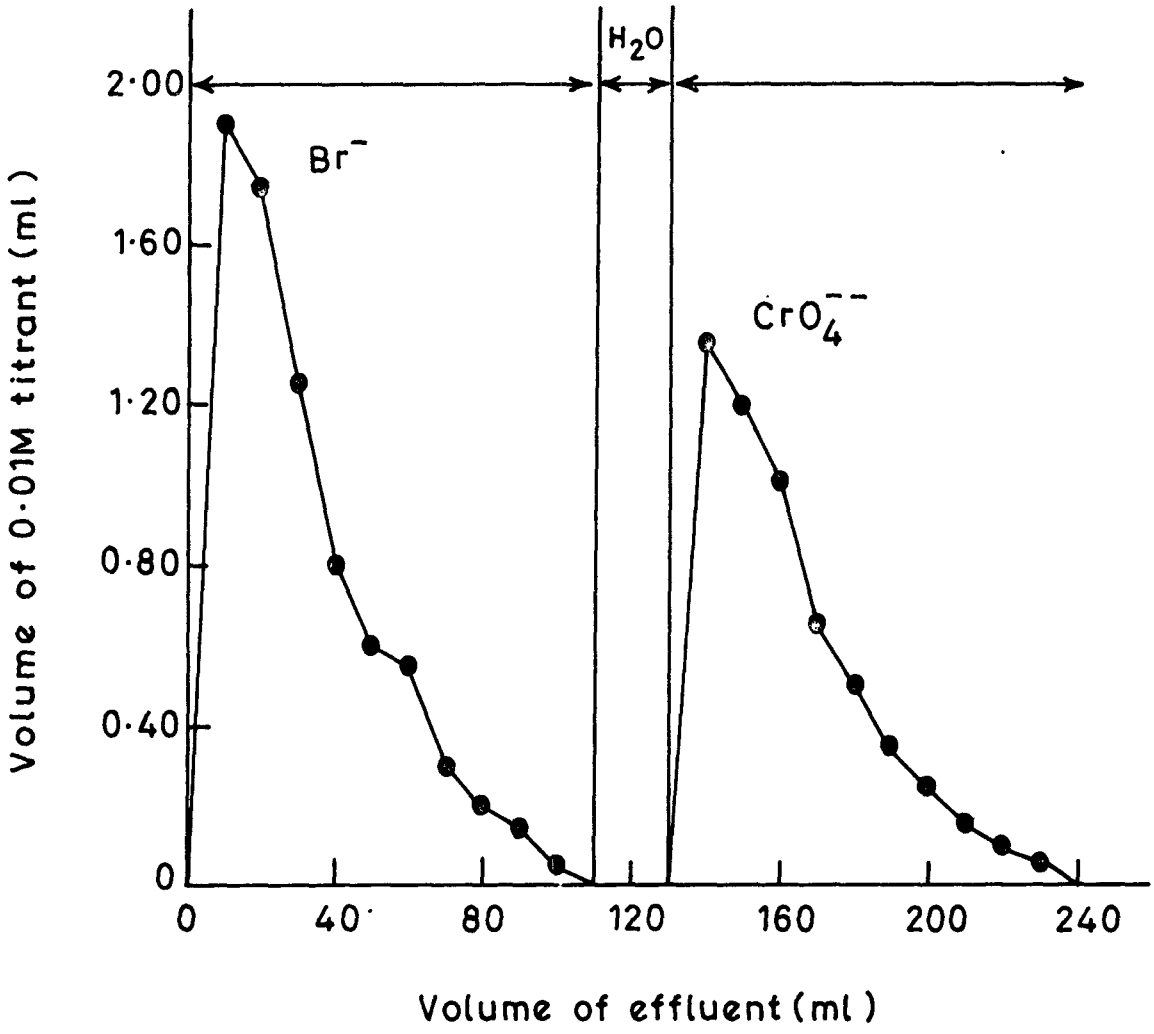

FIG. 37 SEPARATION OF Br^- FROM CrO_4^{--}

TABLE XXX

QUANTITATIVE SEPARATION OF ANIONS ON

FERRIC TRIETHYLAMINE COLUMNS

Sl. No.	Mixture	Eluents	Eluate (ml)	Amount loaded (mg)	Amount found (mg)	% Error
1.	I^-	10^{-4}M NaOH	110	5.588	5.5245	1.15
	CrO_4^{--}	10^{-1}M NaOH	110	6.6234	6.5072	1.75
2.	Br^-	10^{-4}M NaOH	110	6.1607	6.0408	1.94
	$Cr_2O_7^{--}$	10^{-1}M NaOH	100	14.70092	14.48473	1.47
3.	Cl^-	10^{-4}M NaOH	90	1.917	1.846	3.70
	$Cr_2O_7^{--}$	10^{-1}M NaOH	110	14.70092	14.48473	1.47
4.	I^-	10^{-4}M NaOH	100	5.588	5.461	1.27
	SO_4^{--}	10^{-1}M NaOH	90	2.40	2.256	6.0
5.	Br^-	10^{-4}M NaOH	110	6.1607	6.0408	1.94
	CrO_4^{--}	10^{-1}M NaOH	110	6.6234	6.5072	1.75

DISCUSSION

The results of Table XXV show that for complete precipitation to occur, ferric nitrate to triethylamine ratio must be kept 1:4. When ferric triethylamine in H^+ form was kept in contact with a solution of sodium nitrate no release of H^+ was observed. High value of ion exchange capacity towards dichromate ion (1.48) is in accordance with the results of zirconia[5]. The order of capacity for halides is $Cl^- > Br^- > I^-$. The ion exchange capacity of the exchanger decreases as the ionic radii of the halide increases. For other ionic species capacity decreases in the order $Cr_2O_7^{2-} > CrO_4^{2-} > SO_4^{2-}$. The exchanger ferric triethylamine shows anion exchange capacity due to the presence of $-\overset{+}{N}-$ group.

The results presented in Table XXVIII give the effect of temperature on the capacity of exchanger. The capacity decreases with the increase in temperature. At higher temperatures the water molecules and amine molecules are lost from the exchanger and thereby decreasing the capacity.

The results of composition studies show that iron(III) and triethylamine are present in the molar ratio of 1:3 in the exchanger. The results of potentiometric titration curve plotted in Figure 33 reveal that the exchanger iron(III) triethylamine behaves as a monofunctional exchanger.

The infrared spectrum of ferric triethylamine in Figure 34 shows the absorption peaks at different values of wave numbers as given below:

(a) A broad peak ranging from 3300-3550 cm^{-1} is due to the -OH stretching vibrations.

(b) A strong peak at 1380 cm^{-1} is due to C-N vibrations and C-H bending vibrations.

(c) A medium peak lies at 2930 cm^{-1} due to C-H stretching vibrations.

(d) A strong C-C stretching vibration is observed in the frequency range of 1620-1660 cm^{-1}.

(e) A medium C-N bending frequency lies in the frequency range of 1070-1080 cm^{-1}.

(f) A medium peak in the frequency range of 300-640 cm^{-1} is observed due to the metal oxygen bending vibration.

It is quite clear that the exchanger ferric-triethylamine contains amine group and the metal oxygen bond. It confirms that in the formation of this type of exchanger the amine is incorporated with the metal oxide forming the matrix.

The distribution behaviour of anions (Table XXIX) indicates that the Kd values were high when deionized water was used as a medium. Distribution values were less when sodium hydroxide solution was used for studies and they decrease as the concentration of sodium hydroxide solution was increased.

Being a weak anion exchanger, ferric triethylamine has a high affinity for hydroxyl ions, hence anions other than hydroxyl ion showed less uptake in the presence of hydroxyl ions.

Owing to the large differences in the distribution values of various anions many analytically important separations were tried. Separation of CrO_4^{2-} from I^-, $Cr_2O_7^{2-}$ from Br^-, SO_4^{2-} from I^-, $Cr_2O_7^{2-}$ from Cl^- and CrO_4^{2-} from Br^- were successfully achieved (Table XXX). These results also show a high selectivity towards CrO_4^{2-} and $Cr_2O_7^{2-}$ as predicted by Table XXX.

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Ion Exchange Equilibria between Alkali Metals and Hydrogen Ions on Iron(III) Antimonate, an Inorganic Ion Exchanger

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Ion exchange equilibria of alkali metal ions (Li^+, Na^+, K^+ and Rb^+)/H^+ systems have been studied at 30, 40, 50, and 60 °C on iron(III) antimonate as a cation exchanger. The exchange isotherms have been measured for both forward and backward reactions with solutions of ionic strength 0.1 by the batch technique. The isotherms showed S-shaped curves for each exchange system except Li^+/H^+. Selectivity coefficients vary with the equivalent fraction (X_M) of the alkali metal ions in the exchanger and give linear functions against $\bar{X}_M$ in the range from 0—0.40. The selectivity sequence shows $Na^+ < Li^+ < K^+ < Rb^+$. The overall thermodynamic data are evaluated.

Synthetic inorganic ion exchangers have been developed in recent years. The primary aim of most of the studies done in this field has been to achieve the separations. Besides the preparation of new materials and their applications to the separations interest has also been developed towards the study of ion exchange equilibria on these materials. Because of their thermal stability, their rigid structure and consequently negligible swelling, the ion exchange equilibrium studies at different temperatures on these materials will be simpler than on organic ion exchange resins which swell quite appreciably and are prone to thermal instability. The contributions of Larsen Vissers,[1] Ruvarac,[2] Amphlett,[3] Alberti,[4] Nancollas & Dyer[5] are noteworthy in this field. Recently Abe and Sudoh[6,7] described the ion exchange equilibrium studies on antimonic acid for the systems of transition metal ions/H^+ and from these results the appropriate thermodynamic data were derived.

The influence of temperature on the equilibrium between alkaline earth metal ions and hydrogen ion on tantalum arsenate has been described in our earlier paper.[8] Similar studies on the equilibria between alkaline earth metal ions and sodium ion on iron(III) antimonate have also been described.[9] The ion exchange characteristics of iron(III) antimonate are of considerable interest since it behaves as a cation exchanger with different selectivities for cations.[10]

Limiting our attention to series of ions belonging to the same group of the periodic table, that is having the same valency and similar electronic structure, we can study the effects of ion size and hydration upon equilibria eliminating the problem of the influence of eletronic and valency differences. Alkali metal ions can be taken as models for metal ions since they have univalent positive charge. Furthermore, they form inoic bonds and the effect of complex formation can be avoided.

Experimental

The iron(III) antimonate was prepared as described previously.

Determination of Maximum Uptake of Alkali Metal Ions on Iron(III) Antimonate. A 0.1 mol dm^{-3} solution of alkali metal chloride was passed continuously through the iron(III) antimonate column in H^+ form until the change in concentration of the alkali metal ion was negligible between the influent and effluent. The equivalent fraction of H^+ and M^+ in iron(III) antimonate was calculated on the basis of total exchange capacity.

Ion Exchange Equilibria. In the forward reactions the iron(III) antimonate (0.5 g) in H^+ form was immersed in 20 cm^3 of a mixed solution of varying ratio of alkali metal chloride/hydrochloric acid in the conical flasks with intermittent shaking at 30±1, 40±1, 50±1 and 60±1 °C. The ionic strength in the mixed solution was adjusted to 0.1 with hydrochloric acid.

In the reverse reactions the ion exchanger iron(III) antimonate in the respective alkali metal forms corresponding in weight (0.5 g in the hydrogen form) was immersed in the 20 cm^3 of the mixed solution of alkali metal chloride/hydrochloric acid at an ionic strength of 0.1.

Theoretical Aspects. The ion exchange reactions of the univalent alkali metal ions/H^+ exchange systems on iron(III) antimonate can be represented by the following expression:

$$H^+ + M^+ \rightleftharpoons \bar{M}^+ + H^+, \quad (1)$$

where the bar refers to iron(III) antimonate phase and M^+ is the alkali metal ion.

The corrected selectivity coefficient of the above reaction can be defined as:

$$K_c = \frac{\bar{X}_M \cdot X_H}{\bar{X}_H \cdot X_M} \frac{\gamma_H}{\gamma_M}, \quad (2)$$

where K_c is the corrected selectivity coefficient, $\bar{X}_M$ and $\bar{X}_H$ are the equivalent fractions of the metal and H^+ in the exchanger phase, respectively. X_H and X_M are the equivalent fractions of exchanging H^+ and M^+ in the solution phase, respectively. γ_H and γ_M the activity coefficients of hydrogen and the metal in solution respectively. For dilute concentrations the contribution of the activity coefficient ratio (γ_H/γ_M) may be taken as unity.

The thermodynamic equilibrium constant K_a can be calculated using the simplified form of the expression given by Gains and Thomas (11):

$$\ln K_a = \int_0^1 \ln K_c d\bar{X}_M. \quad (3)$$

The change in the free energy of the ion exchange reaction, ΔG° was calculated from the thermodynamic equilibrium constant K_a using the expression:

$$\Delta G^\circ = -RT \ln K_a. \quad (4)$$

The standard enthalpy change, ΔH° has been calculated from the plot of $\log K_a$ against $1/T$.

The standard entropy change, ΔS° is then calculated by the relation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ. \quad (5)$$

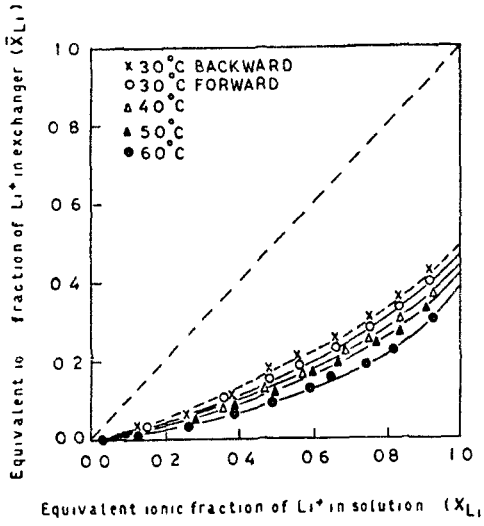

Fig 1 Ion exchange isotherm of Li^+-H^+ exchange iron(III) antimonate

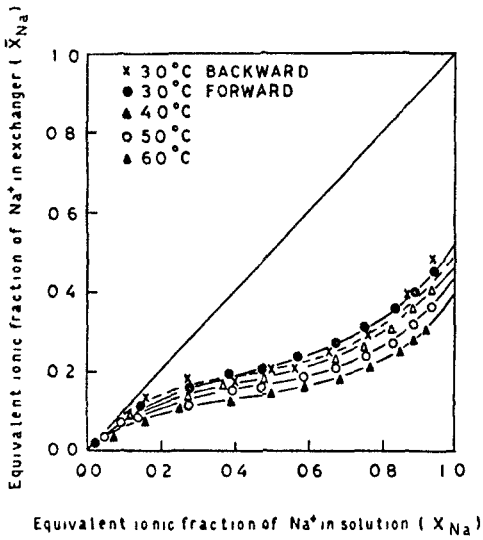

Fig 2 Ion exchange isotherm of Na^+-H^+ exchange on iron(III) antimonate

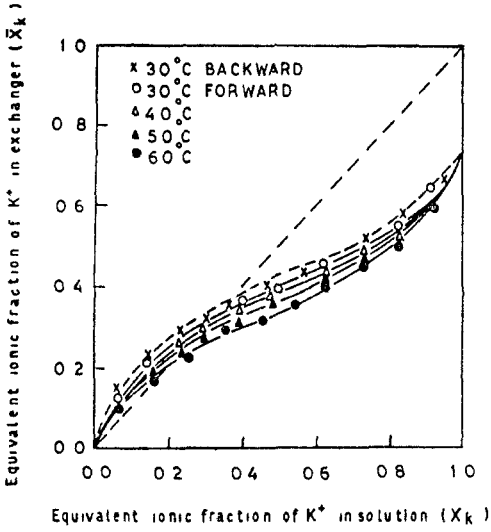

Fig 3 Ion exchange isotherm of K^+-H^+ exchange on iron(III) antimonate

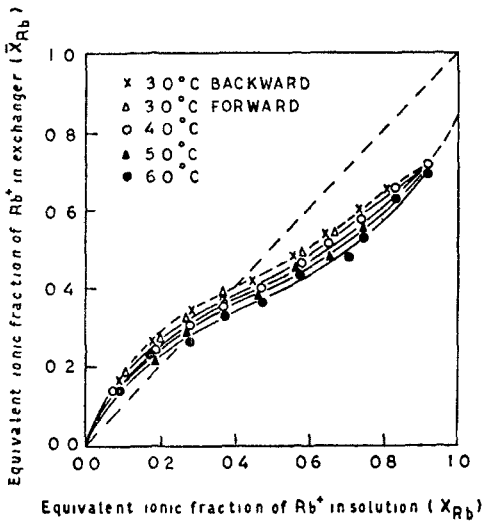

Fig 4 Ion exchange isotherm of Rb^+-H^+ exchange on iron (III) antimonate

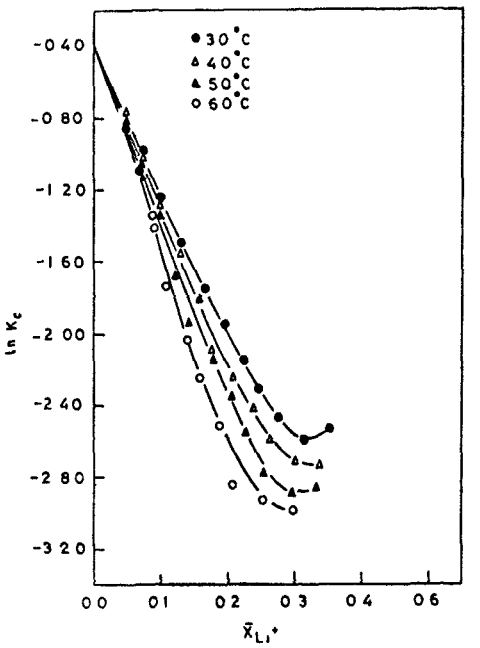

Fig 5 Logarithms of selectively coefficient *vs* ionic fractions of Li^+ in exchanger phase

Results and Discussion

The equilibrium was attained for the forward and backward ion exchange reactions within 6 h shaking

The ion exchange isotherms for the systems Li^+/H^+, Na^+/H^+, K II , and Rb^+/H^+ in a temperature range of 30—60 C are shown in Figs 1 to 4 Ion exchange isotherms have been used to represent graphically experimental data pertinent to ion competition (at different concentration ratios)

For Li^+/H^+ and Na^+/H^+, the isotherms showed that the exchange does not go to completion although entering cation is initially preferred and the degree of exchange gives a value lower than unity For K /H and Rb /H the entering cations show a selectivity reversal with increasing equivalent fraction in the exchanger The isotherms for the reverse exchange are performed only at 30±1 °C and can be plotted

TABLE 1. THERMODYNAMIC PARAMETERS ON IRON(III) ANTIMONATE AT AN IONIC STRENGTH OF 0.1 AND VARIOUS TEMPERATURES

Alkali metal ion	K_a				$\Delta G°$/kJ equiv^{-1}				$\Delta H°$/kJ equiv^{-1} 30—60 °C	$\Delta S°$/J equiv^{-1} deg^{-1}
	30 °C	40 °C	50 °C	60 °C	30 °C	40 °C	50 °C	60 °C		
Li^+	0.08	0.06	0.05	0.04	6.50	7.20	8.10	8.78	17.06	77.60±0.17
Na^+	0.05	0.04	0.03	0.02	7.69	8.74	9.61	10.66	22.17	98.40±0.35
K^+	0.37	0.30	0.27	0.22	2.56	3.15	3.55	4.18	13.85	54.14±0.18
Rb^+	0.60	0.51	0.45	0.40	1.31	1.74	2.17	2.56	11.09	40.98±0.23

TABLE 2. HYPOTHETICAL THERMODYNAMIC DATA ON "ZERO LOADING" OF THE ION EXCHANGE REACTION AT 30 °C

	Li^+	Na^+	K^+	Rb^+
$\ln K_{c\,\bar{X}_M \to 0}$	−0.35	1.50	−2.00	−1.25
$\Delta G°_{\bar{X}_M \to 0}$ kJ equiv^{-1}	0.88	3.79	5.06	3.16
$\Delta H°_{X_M \to 0}$	0.00	0.00	0.00	0.00
$\Delta S°_{\bar{X}_M \to 0}$ J equiv^{-1}	−2.9	−12.5	−16.7	−10.4

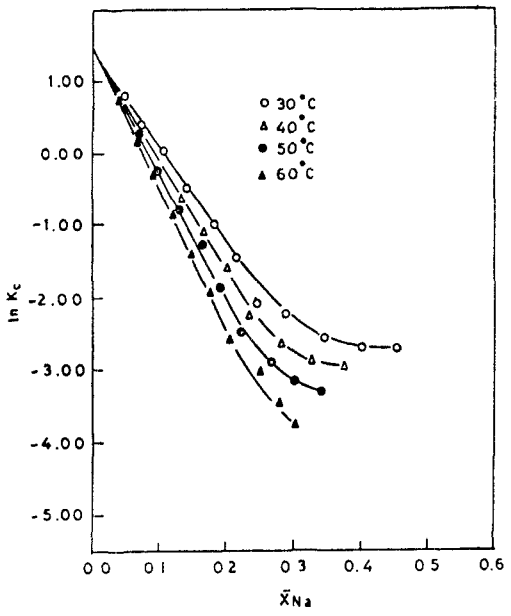

Fig. 6. Logarithms of selectivity coefficient *vs.* ionic fractions Na^+ in exchanger phase.

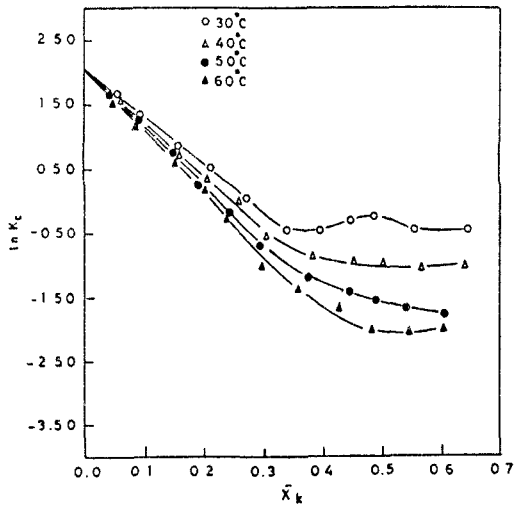

Fig. 7. Logarithms of selectivity coefficients *vs.* ionic fractions of K^+ ions in the exchanger phase.

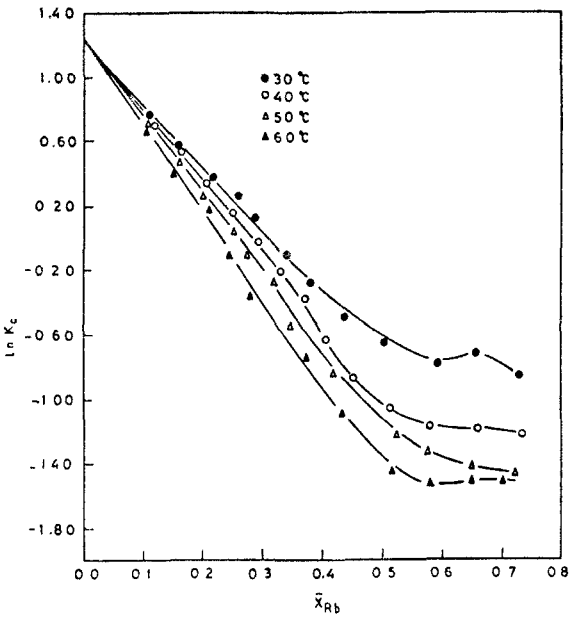

Fig. 8. Logarithms of selectivity coefficients *vs.* ionic fractions of Rb in exchanger phase.

on the cuves of the isotherms for the forwared exchange (Fig. 1 to 4). Thus the ion exchange reactions are reversible throughout the entire range of the compositions studied.

The selectivity of the exchanger can be measured in terms of K_c, which is the quantitative measure of the preferrnce of the exchanger for one ion over another in solution with it. The ln K_c *vs.* X_M which is referred to as Kielland plot gave fairly straight line for all systems at lower values of X_M (Figs. 5 to 8). The linear Kielland plot was also observed for the alkali metal ions H systems on crystalline antimonic acid.

The thermodynamic equilibrium constant K_a was evaluated from Eg. 3 by assuming that the relation between ln K_c *vs.* X_M remains unity over entire range 0 to 1 of X_M. The $\Delta H°$ and $\Delta S°$ showed a corresponding change in their values with the change in temperature since the plots of log K_a *vs.* $1/T$ showed fairly good linearity over the atire range of temperatures studied. The thermodynamic selectivity series was found to be:

$$Na < Li^+ < K^+ < Rb^+.$$

Interpretation of the Selectivity in the Infinitesimal Con-

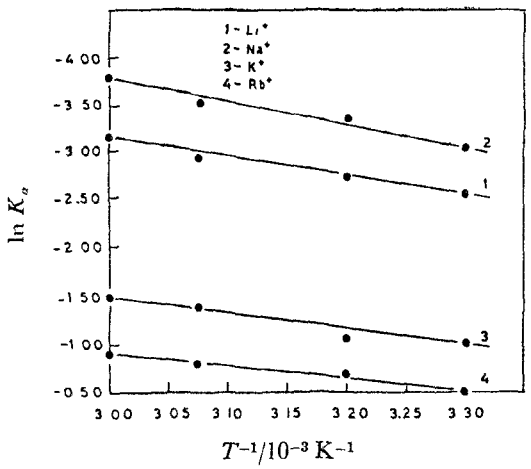

Fig. 9. Temperature dependence of thermodynamic equilibrium constant.

centration of the Alkali Metals. The hypothetical thermodynamic data in infinitesimal concentration were calculated for interpretation of the selectivity of the alkali metal in the trace amounts on iron(III) antimonate and for comparison with those data obtained with other exchangers. The values of $(\ln \bar{K}_c)\bar{X}_M \to 0$ were obtained by extrapolating to "zero loading" (7) of the alkali metals on Fig. 5—8. From these values the hypothetical thermodynamic data were calculated by the similar treatment as for the overall equilibrium constants. The accuracy of these values may be higher than those of the latter. The calculated $(\Delta H^\circ)\bar{X}_M \to 0$ values indicate that there is no enthalpy change in the reaction when metal ion concentration in the solid phase approaches to zero over the entire range of temperatures. While the $(\Delta S^\circ)\bar{X}_M \to 0$ increases with increasing ionic radii of alkali metals except for Rb^+.

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